Supporting Information

Surface-Enhanced Raman Scattering (SERS) Detection of Fluorosurfactants in Firefighting Foams

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1. Raman spectra of ASs

Figure S1 shows the Raman spectra of ASs collected from their solid phase that formed by dropping $\sim 10 \ \mu$ L aqueous solution of $\sim 10 \ m$ M on clean glass surface and drying in air. Note this concentration was much higher than that of dye we used (10 mM vs. 0.01 mM or 5 ppm EV), suggesting the low Raman activity of those ASs.



Figure S1: Raman spectra of ASs. Details see the text.

2. On GO surface



Figure S2: Raman spectra collected from the GO surface. In (a), an Ag substrate was firstly immersed in 5 ppm EV overnight then incubated in a solution of 5 ppm PFOA + 0.5 mg/ml GO overnight. In (b), ~ 10 μ L solution of 5 ppm EV + 0.5 mg/ml GO was dropped and dried on an Ag surface (~2 cm × 2 cm) and then incubated in 5 ppm PFOA overnight.

Figure S2 shows the effect of loading turn. In Figure S2 (a), the EV dye was initially loaded onto the substrate ("Control"). The substrate was subsequently incubated in the solution containing GO and PFOA. The Raman signal of EV weakened (compared to "Control") whilst the Raman signal of GO appeared (1360 cm⁻¹ and 1600 cm⁻¹). The appearance of GO peaks suggests the GO has been deposited onto the substrate surface. The weakened Raman signal of EV is either due to EV de-adsorbing into the GO-PFOA solution in the subsequent incubation process, or due to the shield of GO membrane on the top of EV molecules.

We also deposited the GO and EV solution to form a complex membrane (GO/EV) and used this complex membrane to catch PFOA from the aqueous solution. However, the result is poor again in Figure S2 (b) because EV's weak Raman peaks are shielded by the strong Raman signal of GO. Only when the EV is localised on the outer layer of GO, it can be exposed into the PFOA solution as capture, which means the low loading efficiency. Furthermore, the EV can also be dissolved into the solution and removed from the substrate surface when exposed into the solution.

We thus employed the GO membrane as a SERS substrate to directly collect the immiscible ion-pair of EV-AS from the aqueous solution.