Supporting Information

Metal nanoparticles/MoS_2 SERS-Based Sandwich Immunoassay for α-Fetoprotein Detection

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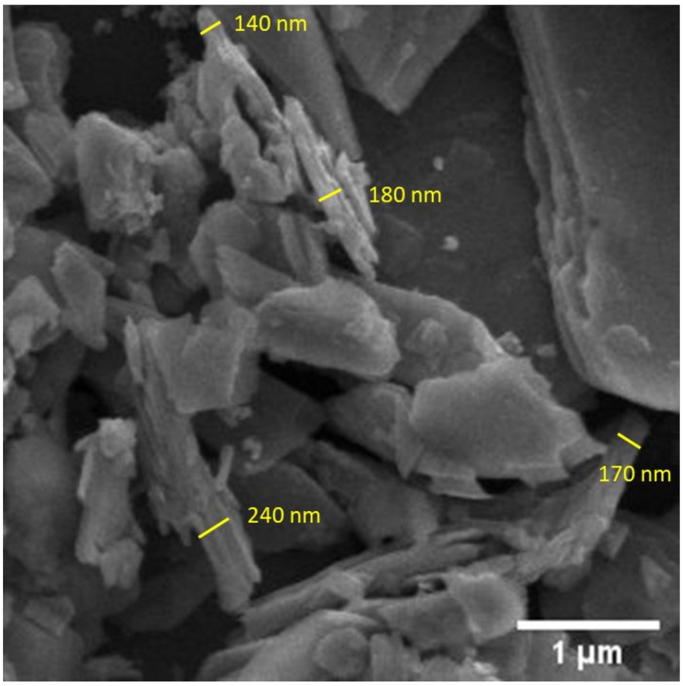


Fig. S1. Representative SEM image of Exf-MoS_2 deposited on SiO_2 with an average thickness of 220 ± 116 nm (Max value: 500 nm, min value: 50 nm) calculated from 17 different measurements.

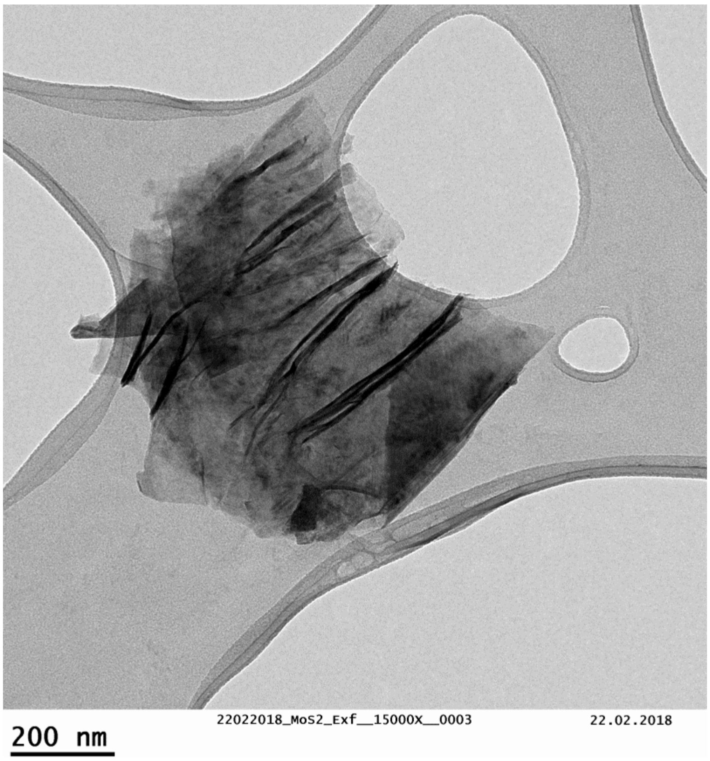


Fig. S2. Representative TEM image of Exf-MoS_2 with an average lateral dimension of 567 ± 239 nm (Max value: 959 nm, min value: 323 nm) calculated from 10 different measurements.

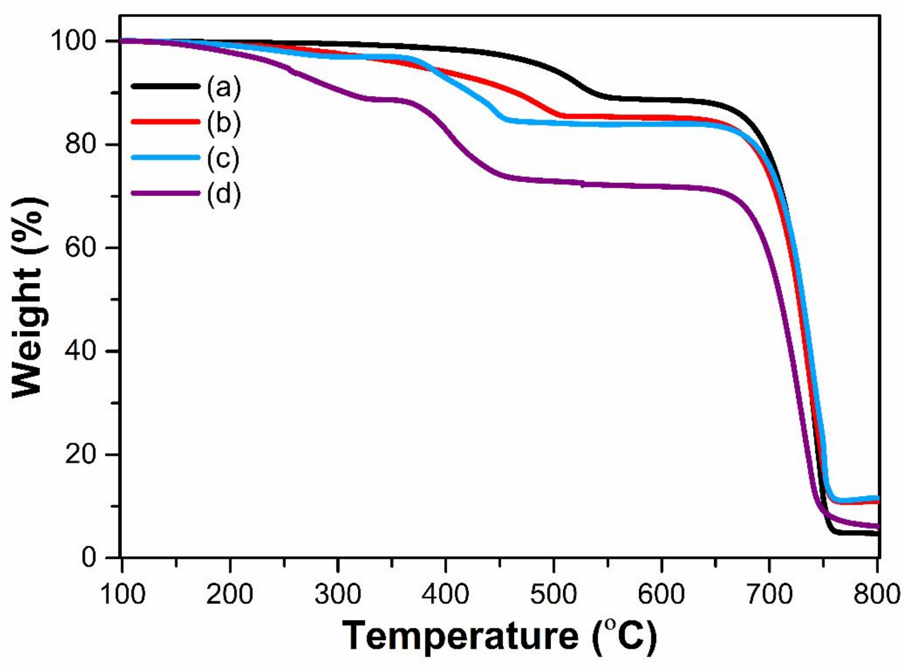


Fig. S3. TGA curves for (a) bulk MoS_2, (b) chemically exfoliated MoS_2, (c) Exf-MoS_2 and (d) mAb functionalized Exf-MoS_2 under air.

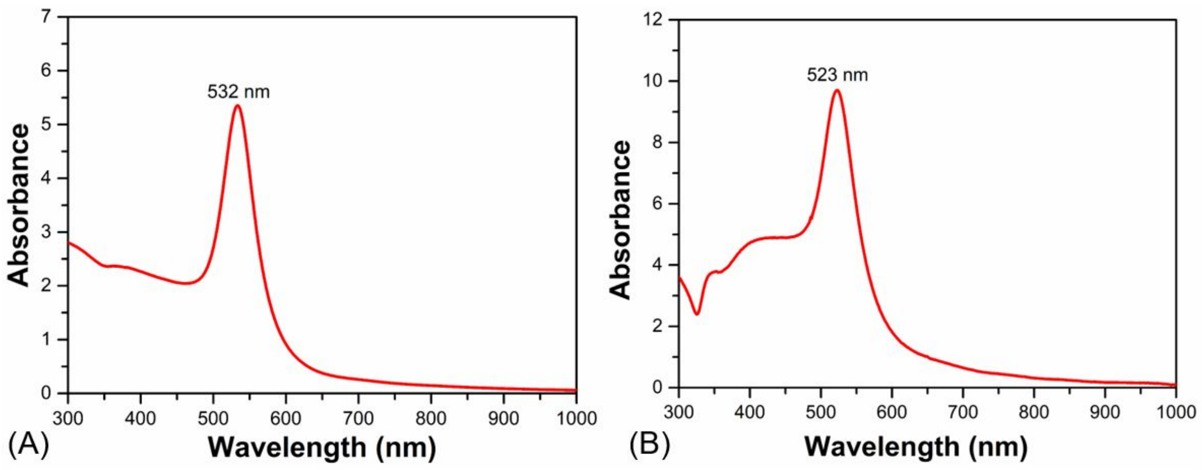


Fig S4. UV-Vis-NIR spectra of initial gold nanospheres in aqueous solution (a) and after silver overgrowth (b).

Raman spectra of bulk MoS_2 (Bulk-MoS_2) and exfoliated MoS_2 by NaK alloy (Exf-MoS_2) excited by 633 nm laser. The two characteristic phonon mode peaks (E_2g at 380 cm^{-1} and A_1g at 404 cm^{-1}) were observed in the Raman spectra of both MoS_2 samples. However, after exfoliation process conducted by NaK alloy, Exf-MoS_2 has the newly appeared low frequency phonon peaks at 180, 200 and 300 cm^{-1}, which correspond to the J_1-J_3 modes, respectively. These characteristic peaks are attributed to the 1T phase. [1,2]

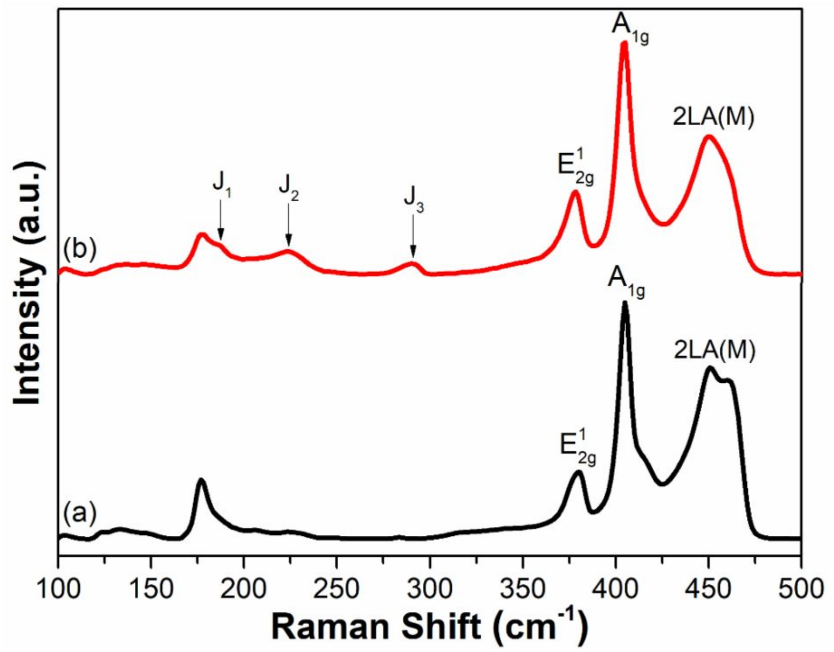


Fig. S5. Raman spectra of (a) Bulk-MoS_2 and (b) Exf-MoS_2.

The ratio 2H/1T phase in Exf-MoS_2 was performed by XPS. The fitted Mo 3d and S 2p core level spectra of Bulk-MoS_2 and Exf-MoS_2 are presented in Figure S3-S4. The binding energies of Mo $3d_{3/2}$ at 229.8 eV and Mo $3d_{5/2}$ at 232.9 eV for Bulk-MoS_2 shifted to the lower energies after exfoliation process, confirming the presence of 1T phase in Exf-MoS_2 as reported by similar studies.[2,3] 1T phase ratio of Exf-MoS_2 was estimated to be ~93% by fitting of Mo 3d core level spectrum.

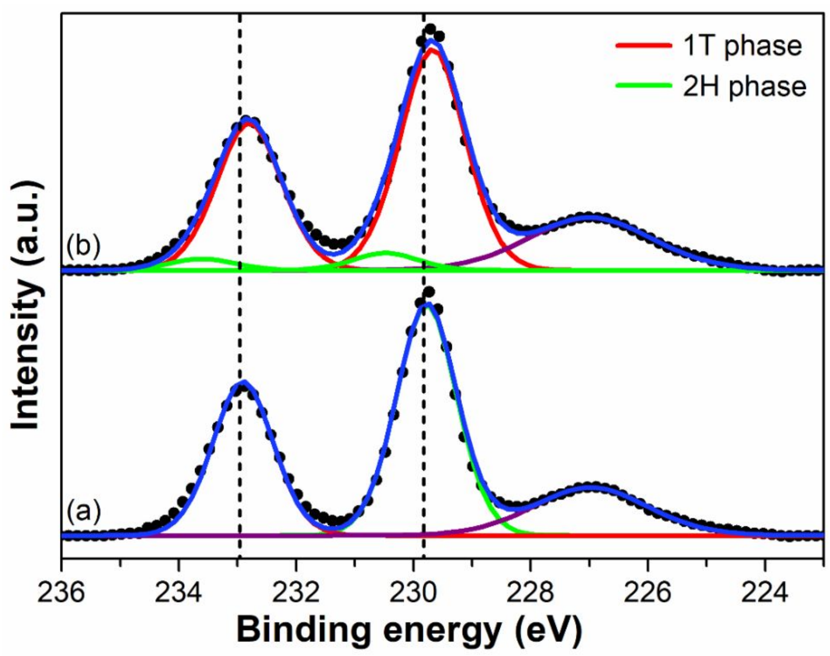


Fig. S6. XPS core level spectra of Mo 3d for (a) Bulk-MoS_2 and (b) Exf-MoS_2.

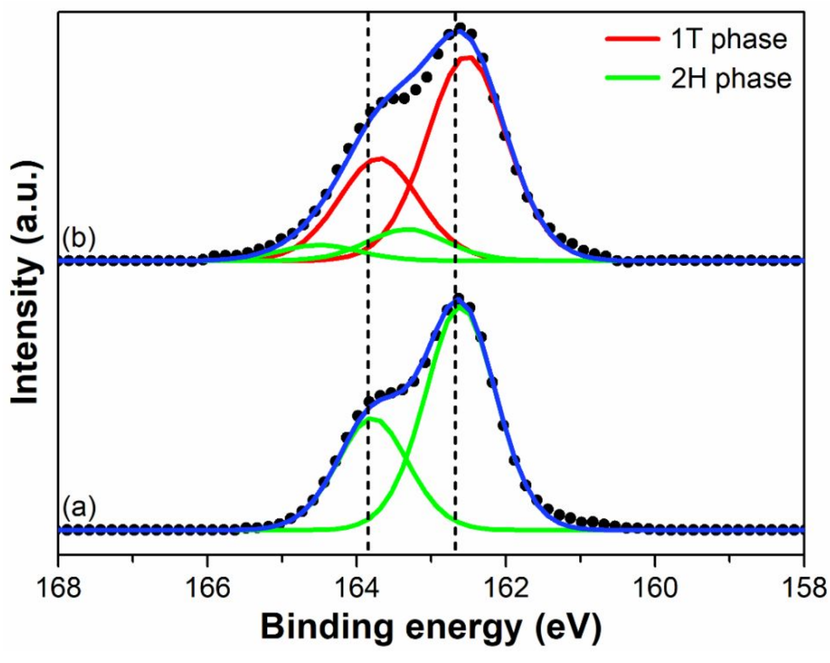


Fig. S7. XPS core level spectra of S 2p for (a) Bulk-MoS_2 and (b) Exf-MoS_2.

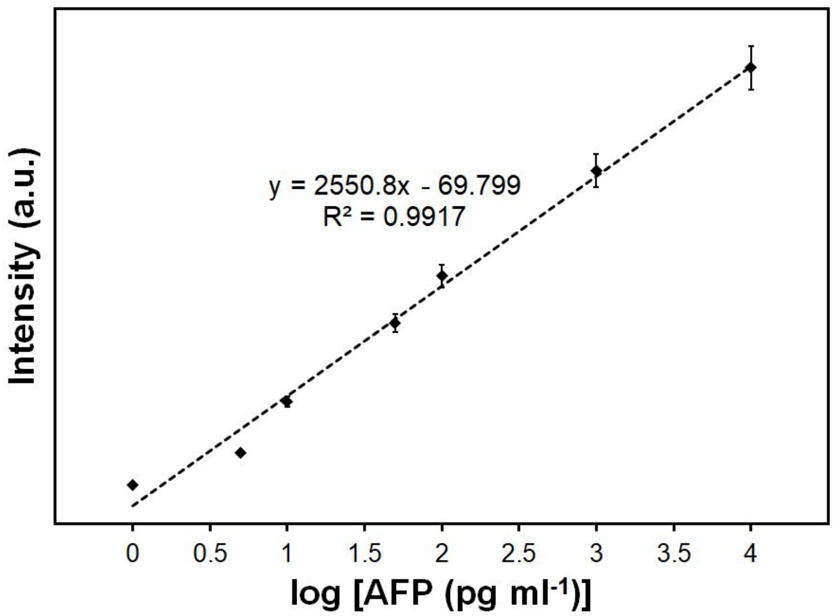


Fig. S8. Linear plot of the SERS peak intensity at 1648 cm^{-1}, as a function of the logarithm of AFP concentration in human serum. (Error bars indicate the standard deviation obtained from five different measurements).

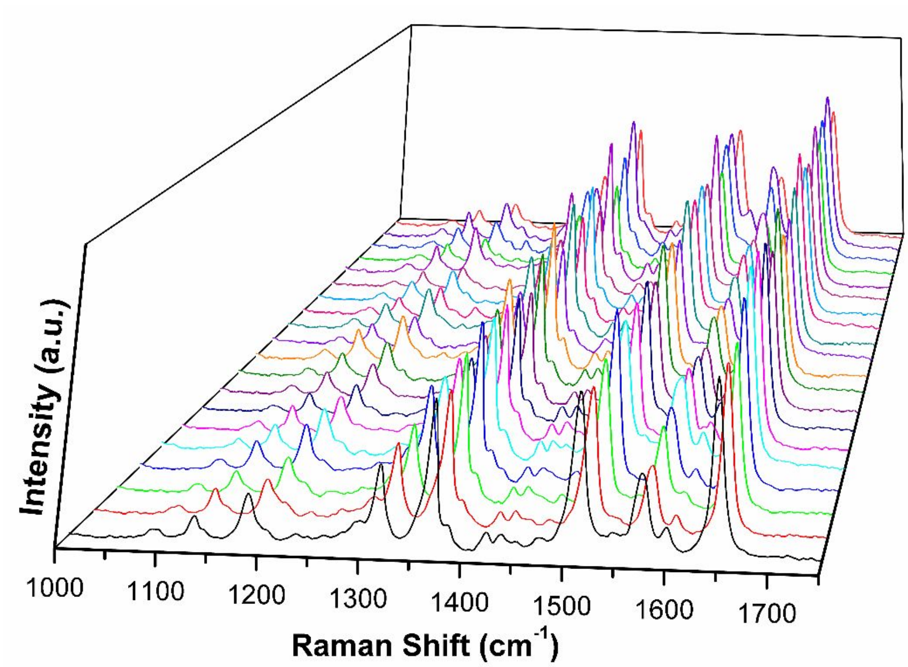
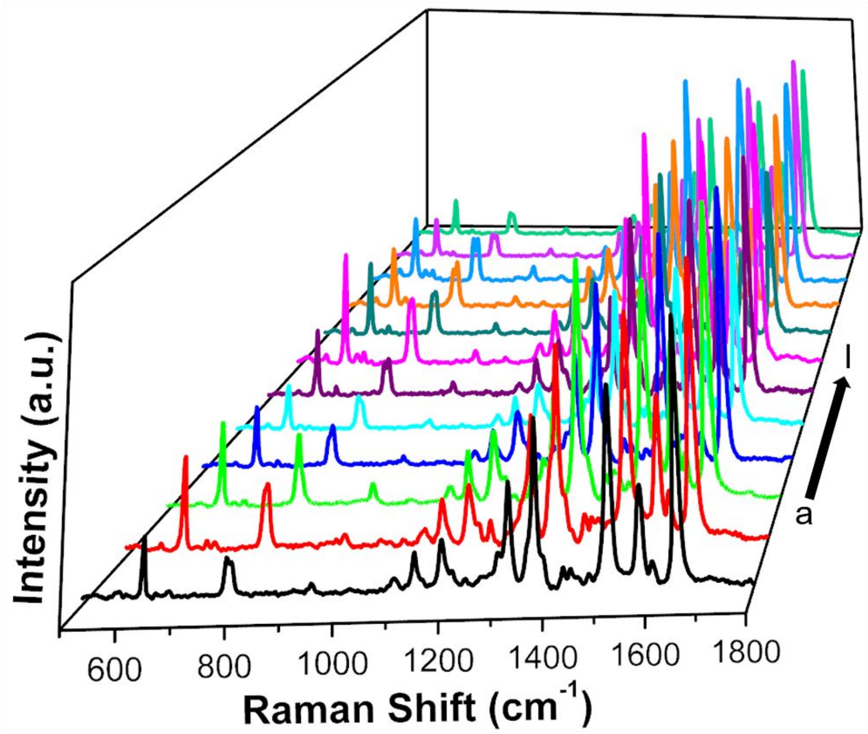


Fig. S9. Reproducibility of SERS spectra for 1.0 ng mL^{-1} AFP collected on 20 randomly selected spots of the developed SERS immunosensor.

A)



B)

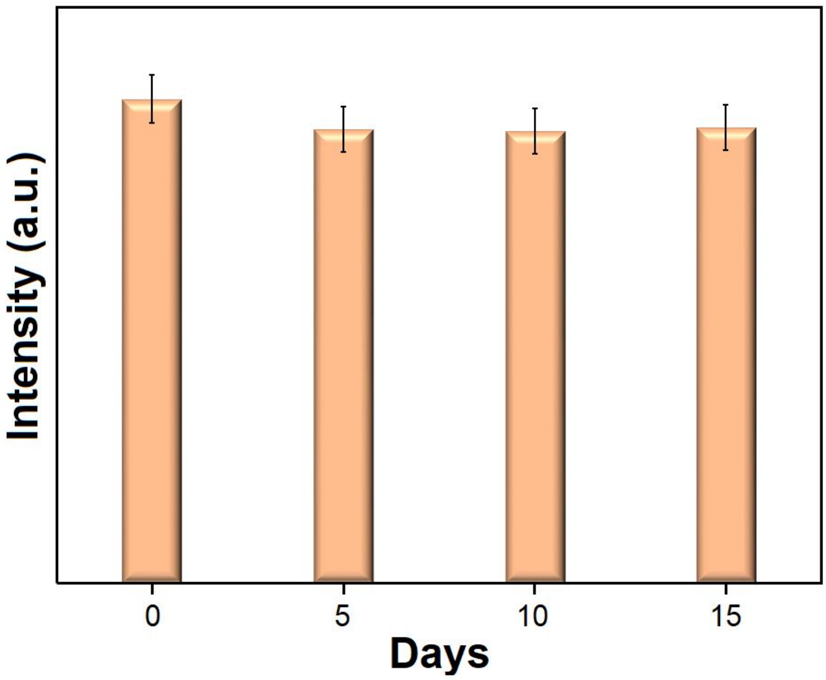


Fig. S10. (A) SERS spectra of R6G at 1.0 ng mL^{-1} AFP collected for 2 weeks from the developed SERS immunosensor (n=3). (B) Histogram of the SERS intensity of the R6G peak at 1648 cm^{-1} for 1.0 ng mL^{-1} AFP *versus* time.

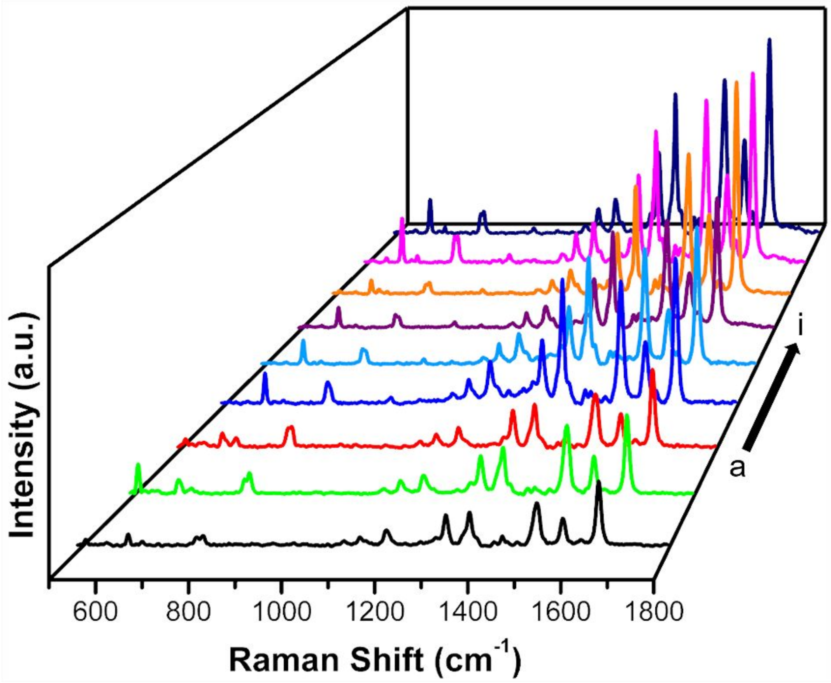


Fig. S11. SERS spectra of R6G at different concentrations of target AFP, ranging from 10 (a-c), 100 (d-f) and 1000 pg mL^{-1} (g-i) on the developed sandwich immunosensor, in human serum.

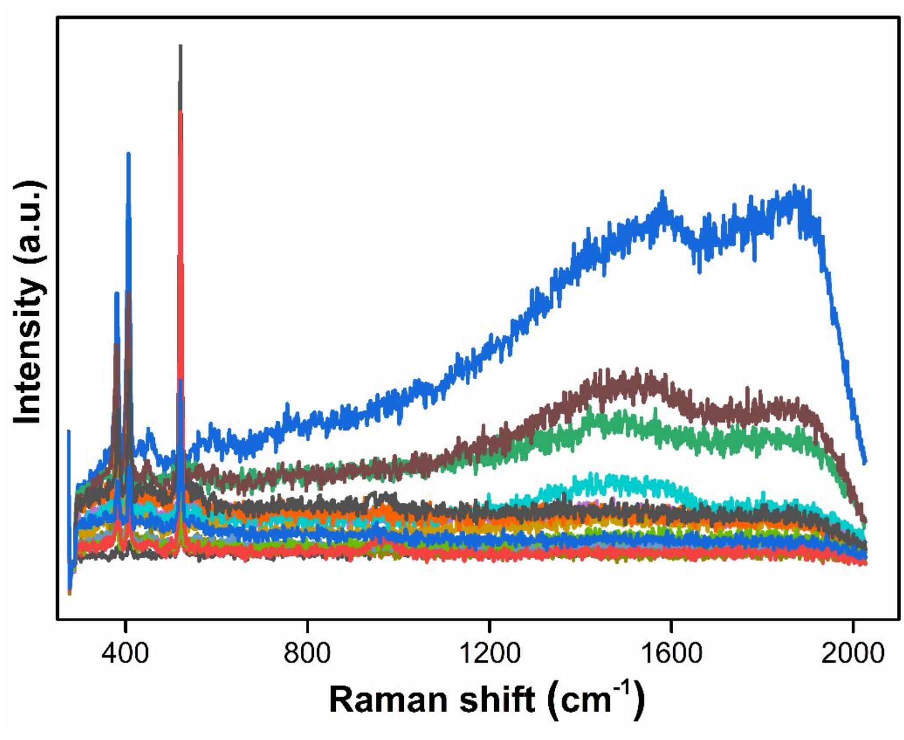


Fig. S12. Raman spectra for the control experiment with zero concentration of AFP in serum. The R6G signals were not detected. The spectra only show the well defined peaks at 380 and 406 cm^{-1} from exfoliated MoS_2 (E^1_{2g} and A_{1g} modes, repectively), and at 995 cm^{-1} from SiO_2.

References

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(2) Benson, E. E.; Zhang, H.; Schuman, S. A.; Nanayakkara, S. U.; Bronstein, N. D.; Ferrere, S.; Blackburn, J. L.; Miller, E. M. Balancing the Hydrogen Evolution Reaction, Surface Energetics, and Stability of Metallic MoS_2 Nanosheets via Covalent Functionalization. *J. Am. Chem. Soc.* **2018**, *140*, 441–450.

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