

Supplementary Information

Label-Free Plasmonic-Based Biosensing Using a Gold Nanohole Array Chip Coated with a Wafer-Scale Deposited WS₂ Monolayer

Lixing Kang^{a,b,c,*†}, Yan Zhang^{d,e†}, Qian Gong^{c†}, Chandreyee Manas Das^{a,b}, Huilin Shao^{d,e}, Daniel Puiu Poenar^{a,b*}, Philippe Coquet^{a,f}, Ken-Tye Yong^g

^aCINTRA CNRS/NTU/THALES, UMI 3288, Research Techno Plaza, 50 Nanyang Drive, Border X Block, Singapore 637553, Singapore

^bSchool of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

^cDivision of Advanced Materials, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China

^dInstitute for Health Innovation & Technology, National University of Singapore, Singapore 117583, Singapore

^eDepartment of Biomedical Engineering, Faculty of Engineering, National University of Singapore, Singapore 117583, Singapore

^fInstitut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), CNRS UMR 8520 – Université de Lille 1, Villeneuve d'Ascq 59650, France

^gThe University of Sydney Nano Institute, The University of Sydney, Sydney, New South Wales 2006, Australia.

† These authors contributed equally to this work.

* Corresponding Authors:

E-mail: EPDPuiu@ntu.edu.sg;

E-mail: lxxkang2013@sinano.ac.cn.

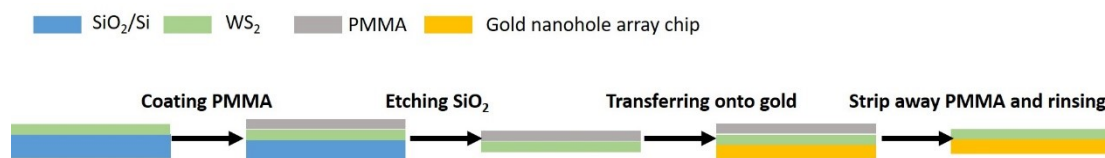


Fig. S1. Schematic description of the process used to transfer the WS₂ film onto the gold nanohole array chip.

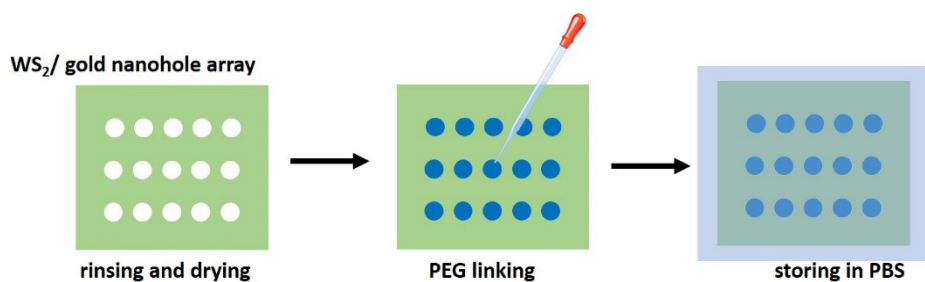


Fig. S2. Schematic description of the WS₂ film functionalization process.

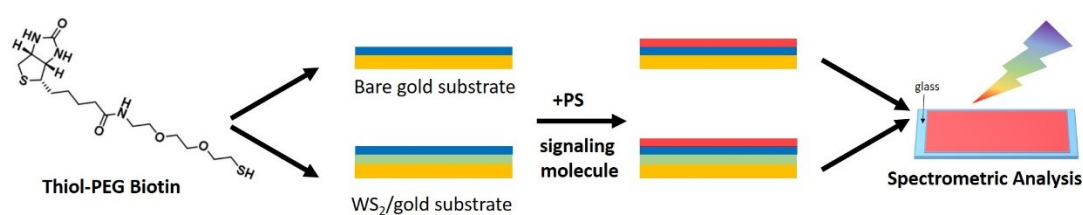


Fig. S3. Schematic description of the biotin-streptavidin coupling process.

Supplementary Table ST1: Measured thicknesses for 10 different WS₂ monolayer samples and their calculated mean and standard deviation values, respectively.

Sample nr.	WS ₂ film thickness [nm]
#1	0.65
#2	0.82
#3	0.64
#4	0.75
#5	0.63
#6	0.86
#7	0.66
#8	0.72
#9	0.89
#10	0.61
Mean value [nm]	0.723
Standard deviation σ [nm]	0.097

Supplementary Table ST2: Measured data for the Raman shifts of 10 different WS₂ monolayer samples and their calculated mean and standard deviation values, respectively.

Sample nr.	Raman shift [cm ⁻¹] for the E ¹ _{2g} peak	Raman shift [cm ⁻¹] for the A _{1g} peak
#1	357.90	422.80
#2	355.88	420.78
#3	356.91	421.80
#4	357.30	422.21
#5	354.92	420.02
#6	355.89	420.29
#7	357.40	422.80
#8	354.93	420.62
#9	355.89	419.80
#10	356.90	421.80
Mean value [cm⁻¹]	356.384	421.292
Standard deviation σ [cm⁻¹]	0.9899	1.071

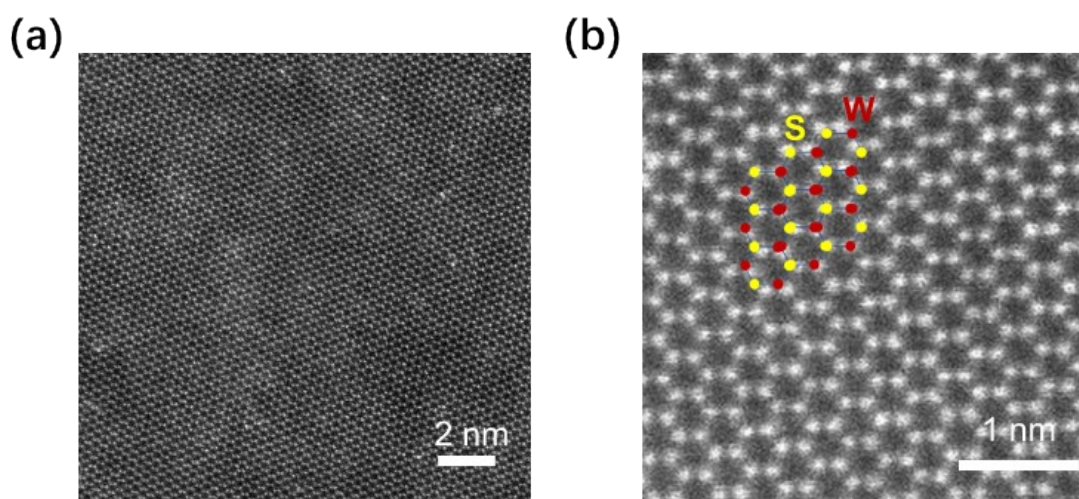


Fig. S6. The TEM morphology of the functionalized WS₂ film.

Supplementary Table ST3: Mean and standard deviation values of normalized performance parameters: SPR transmission intensity, full width at half maximum (FWHM) of the first transmission peak, and detection sensitivity resulted for 10 different sensors, respectively.

Parameter of performance	Mean value (normalized)	Standard deviation σ
Transmissivity	1	0.0186
FWHM	1	0.0133
Sensitivity	1	0.0672

Supplementary Table ST4: Values of all parameters for the linear fitting equation $y = mx + n$ quantifying the extracted variation of the central wavelengths of the main transmission peaks with the RI value of the analyte.

Fitting parameter values	<i>Bare Au nanohole array</i>	<i>WS₂-Au nanohole array</i>
	<i>Second peak</i>	<i>Second peak</i>
Slope (sensitivity) m [nm/RIU]	458.2	563.2
Y-axis intercept n [nm]	624.2	629.9
R^2	0.9934	0.9908

Supplementary Table ST5: Comparative analysis between the performances of previously reported plasmonic biosensors of interest.

Plasmonic Probe	Analyte	LOD	Reference
Light-diffusing fibers SPR sensor	C-reactive protein	1.3×10^{-10} M	1
SPR-sensor chip	Human serum transferrin	4.4×10^{-9} M	2
SPR-sensor chip	Dopamine	10^{-8} M	3
SPR-sensor chip	Tetramethylthiuram disulfide	10^{-6} M	4
SPR-sensor chip	Polystyrene	10^6 beads/mL	This work

References for Supplementary Table ST5:

1. N. Cennamo, C. Trono, A. Giannetti, F. Baldini, A. Minardo, L. Zeni, Tombelli, *S. Sens. Actuators B Chem.* **2021**, 337, 129771.
2. Y. Mayang, X. He, L. Chen and Y. Zhang, *Microchim. Acta* **2017**, 184, 2749–2757.
3. W. Zhu, X. Feng, Z. Liu, M. Zhao, P. He, S. Yang, S. Tang, D. Chen, Q. Guo, G. Wang, G. Ding, *ACS Appl. Mater. Interfaces* **2021**, 13, 23081–23091.
4. M. Zhang, H. Sun, X. Chen, H. Zhou, L. Xiong, W. Chen, Z. Chen, Z. Bao, Y. Wu, *J. Alloy. Compd.* **2021**, 864, 158189.