

## Supporting Information

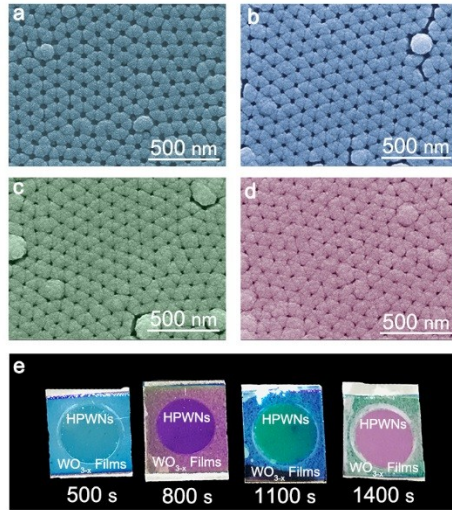
# Plasmon-coupled charge transfer in $\text{WO}_{3-x}$ semiconductor nanoarrays: toward highly uniform silver-comparable SERS platforms

Xiangyu Hou<sup>a</sup>, Xiaoguang Luo<sup>b</sup>, Xingce Fan<sup>a</sup>, Zhaohui Peng<sup>a</sup>, Teng Qiu<sup>\*a</sup>

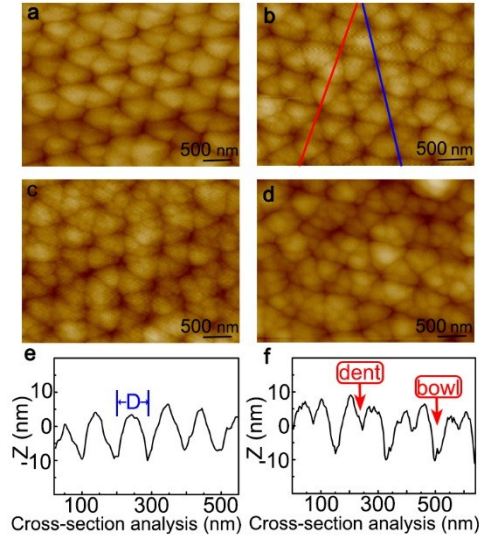
<sup>a</sup>School of Physics, Southeast University, Nanjing, 211189, P.R. China.

<sup>b</sup>Shanxi Institute of Flexible Electronics, Northwestern Polytechnical University, Xi'an, 710072,  
P.R. China.

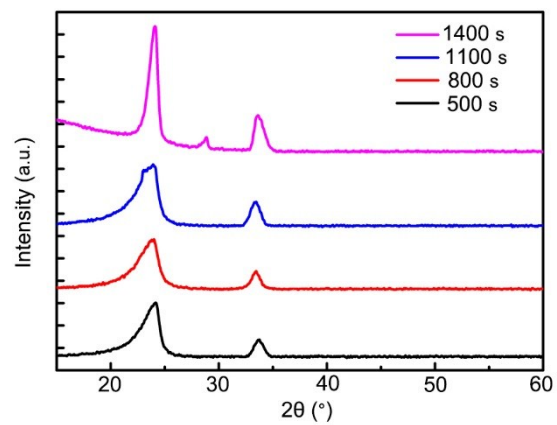
\*E-mail: tqiu@seu.edu.cn



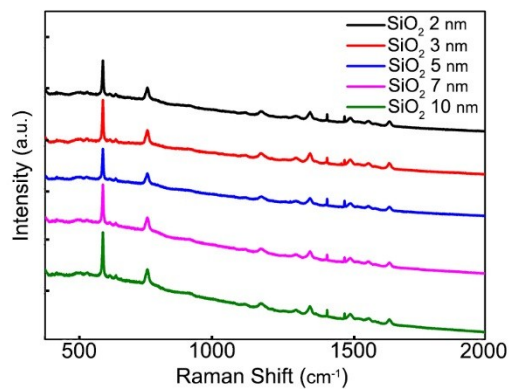
**Fig. S1** A series of HPWNs fabricated by adjusting  $t_w$ . (a-d) A series of SEM images acquired from HPWNs formed under different constant  $t_w$ : (a) 500, (b) 800, (c) 1100 and (d) 1400 s. (e) Optical image of (a-d).



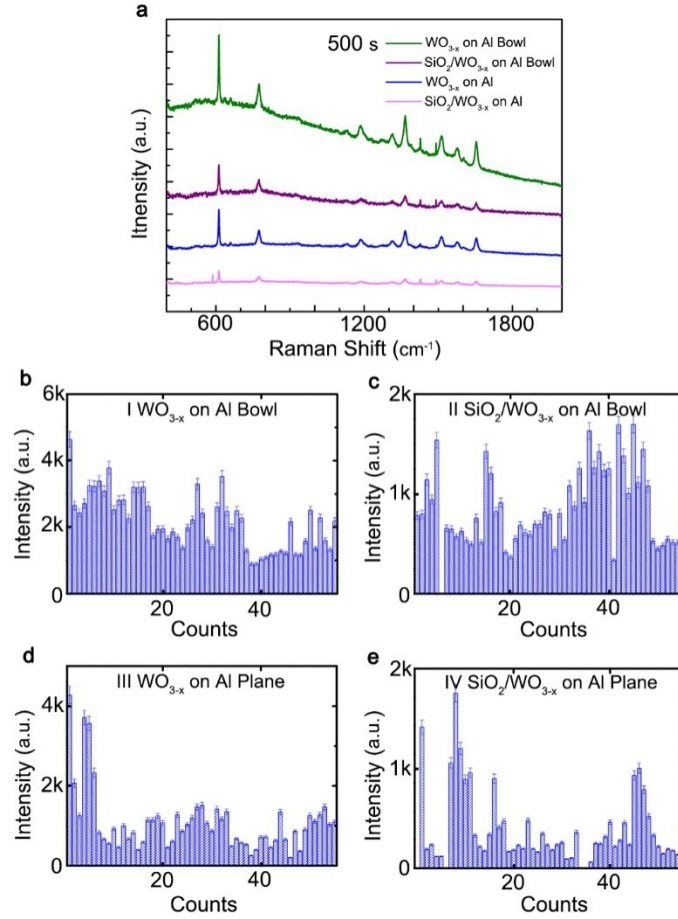
**Fig. S2** D and L analysis of HPWNs. (a-d) A series of AFM images acquired from (Figure S1a-S1d). (e, f) Cross-section analysis along the blue and red lines in (b), respectively. The value of D was acquired from the distance of two adjacent peak valleys in (e). The value of L was calculated by the vertical line of each petal on HPWNs acquired from the distance between dent and adjacent bowl in (f).



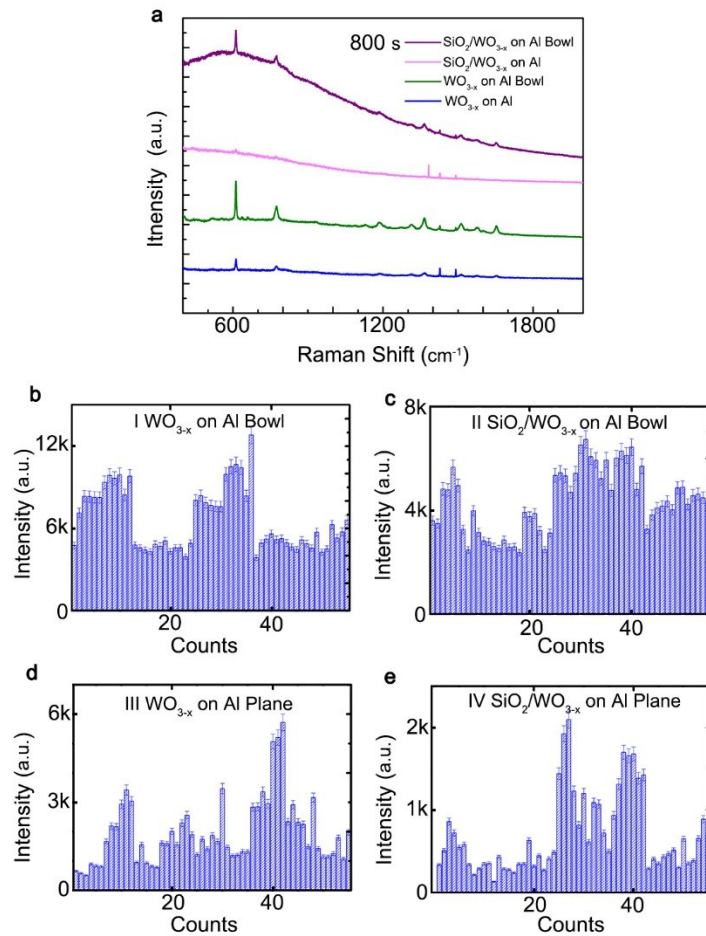
**Fig. S3** XRD spectra of HPWNs.



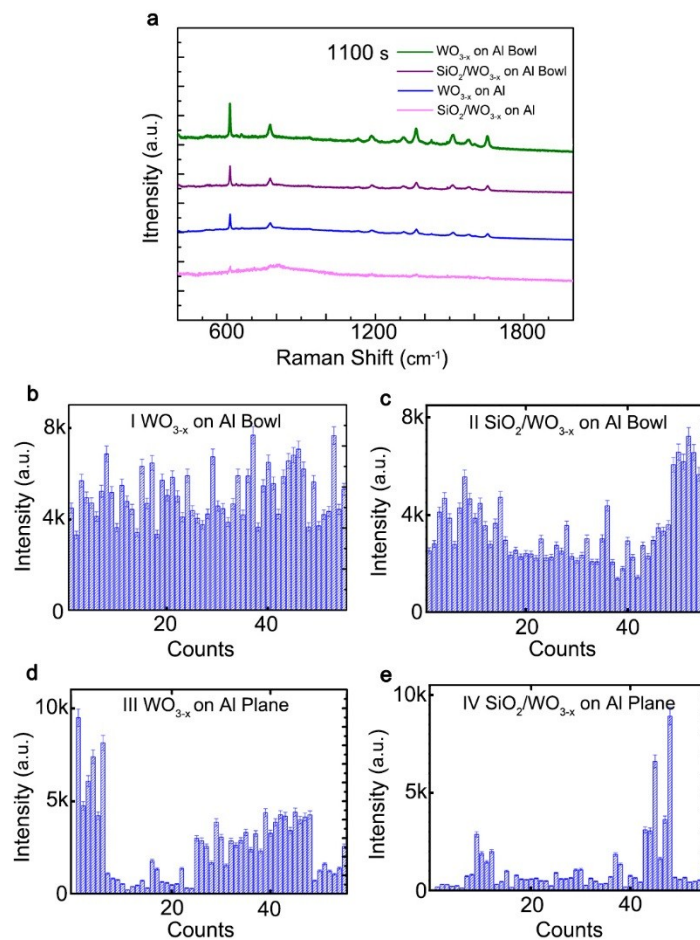
**Fig. S4** SERS measurements of R6g with different thickness of SiO<sub>2</sub> coated on HPWNs. The concentration of R6g was 10<sup>-5</sup> M and the thickness of SiO<sub>2</sub> was 2, 3, 5, 7, and 10 nm, respectively.



**Fig. S5** SERS measurements of R6g on the double-switches experiment with  $t_w=500$  s. (a) Raman spectra of R6g ( $10^{-5}$  M) collected on I-IV substrates. (b-e) Intensities of Raman signals of P1 ( $612\text{ cm}^{-1}$ ) vibration mode of R6g molecule on I-IV substrates. Data were acquired by 55 points from a total of five samples for each substrates.

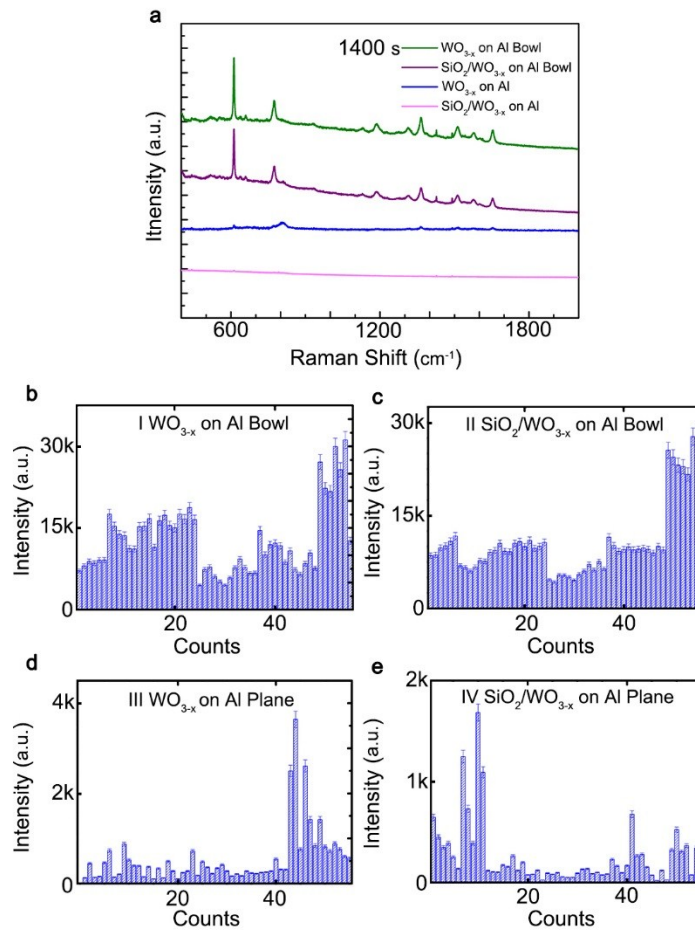


**Fig. S6** SERS measurements of R6g on the double-switches experiment with  $t_w=800$  s. (a) Raman spectra of R6g ( $10^{-5}$  M) collected on I-IV substrates. (b-e) Intensities of Raman signals of P1 ( $612\text{ cm}^{-1}$ ) vibration mode of R6g molecule on I-IV substrates. Data were acquired by 55 points from a total of five samples for each substrates.

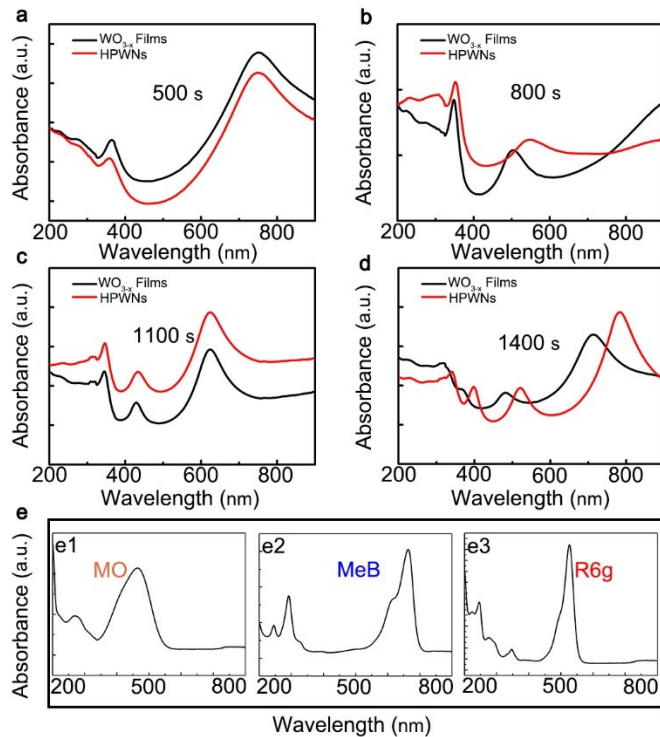


**Fig. S7** SERS measurements of R6g on the double-switches experiment with  $t_w=1100$  s. (a) Raman spectra of R6g ( $10^{-5}$  M) collected on I-IV substrates. (b-e) Intensities of Raman signals of P1 ( $612\text{ cm}^{-1}$ ) vibration mode of R6g molecule on I-IV substrates. Data were acquired by 55 points from a total of five samples for each substrates.





**Fig. S8** SERS measurements of R6g on the double-switches experiment with  $t_w=1400$  s. (a) Raman spectra of R6g ( $10^{-5}$  M) collected on I-IV substrates. (b-e) Intensities of Raman signals of P1 ( $612 \text{ cm}^{-1}$ ) vibration mode of R6g molecule on I-IV substrates. Data were acquired by 55 points from a total of five samples for each substrates.



**Fig. S9** UV-vis absorption spectra. (a-d) A series of UV-vis absorption spectra acquired from HPWNs compared with  $\text{WO}_{3-x}$  films by adjusting  $t_w$  (500 s, 800 s, 1100 s and 1400 s, respectively). The energy changes were -0.05646, 0.197544, 0.0333 and 0.197135 eV, respectively. (e1-e3) UV-vis absorption spectra of a water solution of MO ( $10^{-4}$  M), MeB ( $10^{-5}$  M) and R6g ( $10^{-5}$  M), respectively.

**Table S1** Detection of probe molecules on HPWNs by specific rules. The prediction of probe molecules could be detected on HPWNs from literatures by specific rules.

<b>Analyte</b>	<b>Excited wavelength (nm)</b>	<b>SERS- PICT</b>	<b>LSPR</b>	<b><math>\mu_{\text{mol}}</math></b>	<b>SERS enhancement</b>	<b>Reference</b>
<b>RhB</b>	532nm	on	on	on	√	1,2
<b>MB</b>	633nm	off	on	on	√	1,3,4
<b>4-Mpy</b>	532nm	on	on	off	√	5,6
<b>4-MBA</b>	532nm	on	on	off	√	3,7
<b>PA</b>	532nm	on	on	off	√	8-10
<b>TNT</b>	532nm	on	on	off	√	10-12

## REFERENCES

- 1 S. Shi, M. A. Gondal, A.A. Al-Saadi, R. Fajgar, J. Kupcik, X. F. Chang, K. Shen, Q. Y. Xu and Z. S. Seddigi. *J. Colloid Interface Sci.*, 2014, **416**, 212–219.
- 2 P. H. Shao, J. Y. Tian, Z. W. Zhao, W. X. Shi, S. S. Gao and F. Y. Cui. *Appl. Surf. Sci.*, 2015, **324**, 35–43.
- 3 H. Wu, H. Wang and G. Li. *Analyst.*, 2017, **142**, 326–335.
- 4 S. Naraginti, F. B. Stephen, A. Radhakrishnan and A. Sivakumar. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 2015, **135**, 814–819.
- 5 X. Y. Su, H. Ma, H. Wang, X. L. Li, X. X. Han and B. Zhao. *Chem. Commun.*, 2018, **54**, 2134–2137.
- 6 J. R. Lombardi. *Faraday Discuss.*, 2017, **205**, 105–120.
- 7 W. N. Liu, T. Yang, J. H. Chen, Y. Z. Chen, X. M. Hou, X. M. Han and K. C. Chou. *Phys. Chem. Chem. Phys.*, 2016, **18**, 27572–27576.
- 8 A. Deshmukh, S. Bandyopadhyay, A. James and A. Patra. *J. Mater. Chem. C.*, 2016, **4**, 4427–4433.
- 9 S. Hussain, A. H. Malik, M. A. Afroz and P. K. Iyer. *Chem. Commun.*, 2015, **51**, 7207–7210.
- 10 Z. Hu, B. J. Deibert and J. Li. *Chem. Soc. Rev.*, 2014, **43**, 5815–5840.
- 11 J. H. Qin, B. Ma, X. F. Liu, H. L. Lu, X. Y. Dong, S. Q. Zang and H. W. Hou. *J. Mater. Chem. A.*, 2015, **3**, 12690–12697.
- 12 P. Wu, C. Xu, X. Hou, J. J. Xu and H. Y. Chen. *Chem. Sci.*, 2015, **6**, 4445–4450.