

Supplementary Materials for

Ag@BiOCl Super-hydrophobic Nanostructure for Enhancing SERS Detection Sensitivity

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Section S1. CA of Si substrate before and after surface modification

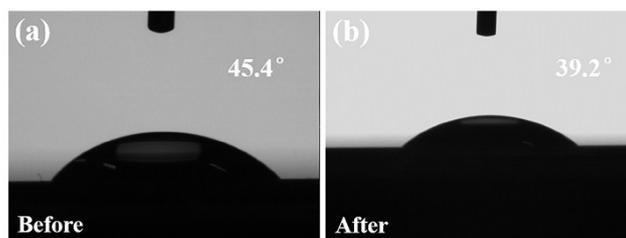


Fig. S1 (a-b) CA of Si substrate before and after surface modification.

Section S2. SEM images and Raman spectra of R6G molecules for Ag@BiOCl NSs with different Ag depositing times

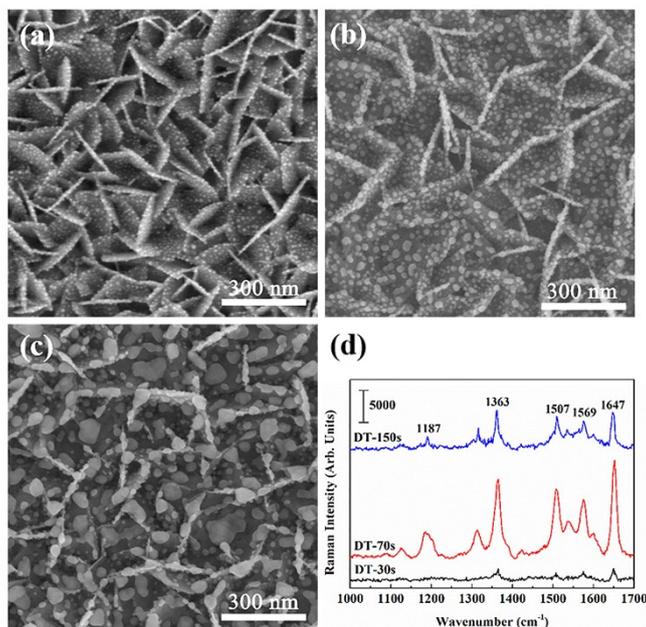


Fig. S2 SEM images of Ag@BiOCl with different Ag depositing times: (a) 30s, (b) 70s and (c) 150s.

(d) The corresponding Raman spectra of Ag@BiOCl NSs of R6G (10⁻⁷ M) solution with different Ag depositing times.

Section S3. Comparison of Raman spectra of surface modified BiOCl NSs and Si substrate

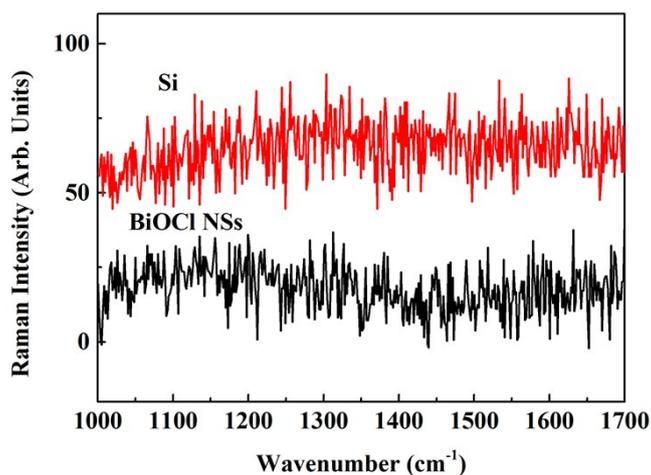


Fig. S3 Raman spectra of BiOCl NSs substrate with surface modification and clean Si substrate.

Section S4. Raman spectra of R6G molecules for Ag@BiOCl NSs substrate and Ag substrate

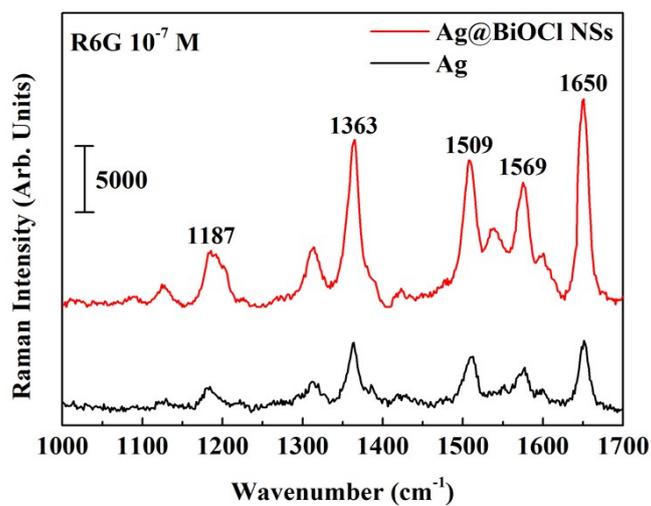


Fig. S4 Raman spectra of R6G solution (10⁻⁷ M) for Ag@BiOCl NSs and Ag nanoparticles with the same sputtering time.

Section S5. Raman spectra of R6G molecules for Si substrate

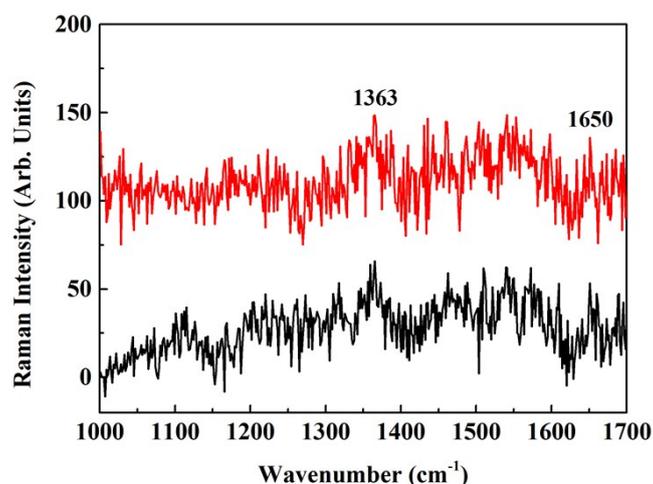


Fig. S5 Raman spectra of R6G molecules at a concentration of 10^{-3} M for Si substrate as the non-enhanced substrate. The averages value of two peak intensities are used to calculate experimental SERS EFs.

Section S6. Calculation of experimental SERS enhancement factors

The Raman measurement experiment of the SERS substrate and that of the non-SERS substrate are performed under exactly identical experimental conditions. The power excitation laser is 514.5 nm and acquisition time is 20 s. We dropped 10.0 μ L R6G solution (1.0×10^{-3} M) on non-SERS substrate for the collection of the Raman signal. The dried area was 11.28 mm² on the Si substrate. N_{Vol} of 4.19×10^{20} in the laser spot was estimated based on the focusing area. The same method was used to drop the concentration of 10^{-9} M R6G solution on SERS substrate and got a 8.09 mm² round area. N_{Surf} of 5.84×10^{14} in the laser spot was estimated based on the focusing area. Raman shifts of 1363 cm⁻¹ and 1650 cm⁻¹ were chosen to calculate the $EF_{\text{SERS}} \cdot I_{\text{SERS}}$ is 1207 at 1363 cm⁻¹ and 909.65 at 1650 cm⁻¹, which are peak intensities from Fig. 4b. I_{RS} is 69.60 at 1363 cm⁻¹ and 57.02 at 1650 cm⁻¹, which are average values from Fig. S5. Based on above assumptions and

calculations, we obtained the average SERS EF of Ag@BiOCl NSs chip is evaluated to be 1.25×10^7 at 1363 cm^{-1} and 1.15×10^7 at 1650 cm^{-1} .

Section S7. FDTD simulation of Ag@BiOCl NSs with different incident light polarization angles.

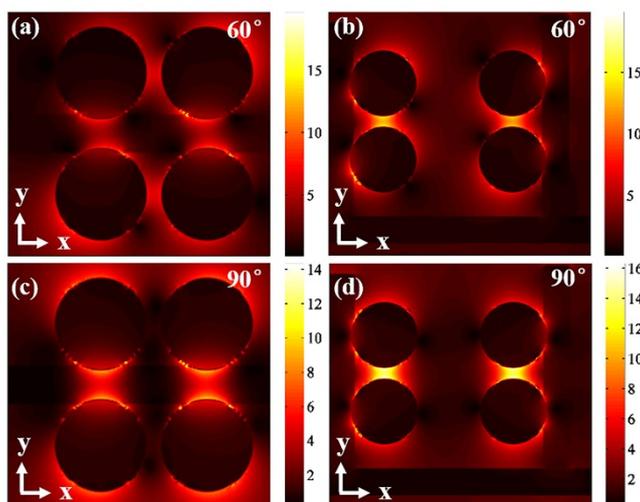


Fig. S6 The normalized electric field intensity ($|E|/|E_0|$) distribution of (a-c) between adjacent Ag particles on the single side of BiOCl NSs and of (b-d) Ag particles on adjacent BiOCl NSs with incident light polarization angles of 60 and 90 deg, respectively.

Section S8. Comparison between existing SERS sensors and Ag@BiOCl NSs SERS chip

Table S1. Comparison between existing SERS sensors and Ag@BiOCl NSs SERS chip

SERS structure	CA	EFSERS	Probe molecule	Detection limit	Reference
Zinc oxide nanorods array	152°	—	4-ATP	$5 \mu\text{l}$	Ref [1]
Silver capped polystyrene nanotube array	110°	1.6×10^6	4-ABT	$\sim 400 \text{ ppt}$	Ref [2]
AgNPs on filter paper	150°	—	melamine	1 ppm	Ref [3]
Cu nanoparticle-coated copper vanadate nanoribbons	—	1.2×10^6	R6G	0.25 M	Ref [4]

Ag@BiOCl nanosheets	157.4°	1.25×10 ⁷	R6G	10 ⁻⁹ M	This work
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References

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- [2] P. Lovera, N. Creedon, H. Alatawi, M. Mitchell, M. Burke, A. J. Quinn, A. O'Riordan, *Nanotechnology* 2014, **25**, 175502-175507.
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