## Ultrasensitive plasmonic biosensors based on halloysite nanotubes/MoS<sub>2</sub>/black

## phosphorus hybrid architectures

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Fig. S1 Variations of (a) reflectance and (b) phase with respect to the incident angle by changing the layer number of MoS<sub>2</sub> film. The refractive index of initial calibration biosensing medium is  $n_s = 1.333$  RIU. Layer number of BP, thicknesses of HNTs and gold films are 3L, 400 and 40 nm, respectively.

## Transfer matrix method for calculating the decay curve of evanescent field

Within this framework of transfer matrix method,<sup>1,2</sup> it is assumed that there are two perpendicular magnetic field components with amplitudes  $B_{jup}$  and  $B_{jdown}$  to propagate up (positive *z*) and down (negative *z*) in the *j*th medium, respectively. In the semi-infinite materials there is only one wave going in positive *z* after the *N*+1 boundary and negative *z* before the first boundary. Then the boundary conditions of the electromagnetic field can be described via using a matrix form as AB = 0 where

$$A = \begin{pmatrix} -1 & e^{-ik_{z1}d_{1}} & e^{ik_{z1}d_{1}} & 0 & \cdots & 0 \\ 0 & -1 & -1 & e^{-ik_{z2}d_{2}} & e^{ik_{z2}d_{2}} & 0 & \cdots & 0 \\ \cdots & & & & \ddots & \\ 0 & 0 & 0 & \cdots & 0 & -1 & -1 & 1 \\ \frac{k_{z0}}{n_{0}^{2}} & -\frac{k_{z1}}{\eta_{1}^{2}} e^{-ik_{z1}d_{1}} & \frac{k_{z1}}{\eta_{1}^{2}} e^{ik_{z1}d_{1}} & 0 & \cdots & 0 \\ 0 & \frac{k_{z1}}{\eta_{1}^{2}} & -\frac{k_{z1}}{\eta_{1}^{2}} & -\frac{k_{z2}}{\eta_{2}^{2}} e^{-ik_{z2}d_{2}} & \frac{k_{z2}}{\eta_{2}^{2}} e^{ik_{z2}d_{2}} & 0 & \cdots & 0 \\ 0 & \frac{k_{z1}}{\eta_{1}^{2}} & -\frac{k_{z1}}{\eta_{1}^{2}} & -\frac{k_{z2}}{\eta_{2}^{2}} e^{-ik_{z2}d_{2}} & \frac{k_{z2}}{\eta_{2}^{2}} e^{ik_{z2}d_{2}} & 0 & \cdots & 0 \\ \cdots & & & & \cdots & & \\ 0 & 0 & 0 & \cdots & 0 & \frac{k_{zN}}{\eta_{N}^{2}} & -\frac{k_{zN}}{\eta_{N}^{2}} & \frac{k_{zN+1}}{\eta_{N+1}^{2}} \end{pmatrix}$$

$$B = \begin{pmatrix} B_{0up} \\ B_{1up} \\ B_{1down} \\ B_{2up} \\ \vdots \\ B_{N-1down} \\ B_{Nup} \\ B_{Ndown} \\ B_{N+1down} \end{pmatrix}$$
(2)

In the above expressions, A is a  $(2N+2) \times (2N+2)$  matrix and B is a vector of length (2N+2). The complex wave vector  $k_j$  holds the momentum conservation  $k_j^2 = k_x^2 + k_{zj}^2$  where  $k_x$  is the tangential component (along the surface) for all materials and  $k_{zj}$  is the perpendicular component varying dependent on the *j*th material. The eigen mode of the system occurs when the determinant of the matrix A equals 0 with a nonzero vector B. Then it is possible to solve the real and imaginary parts of  $k_x$  for each frequency of interested plasmonic surface wave.

Once the  $k_x$  value is found, the corresponding field coefficients can be solved by using the same equations. The overall field amplitude is arbitrary, so one can assign a value to one coefficient, such as  $B_{0up} = 1$ , and get a new system of equations  $A_2B_2 = C$ , with  $A_2$  of size  $(2N+2) \times (2N+1)$ ,  $B_2$  of length (2N+1) in length and *C* of length (2N+2). The new matrix  $A_2$  becomes

$$A_{2} = \begin{pmatrix} e^{-ik_{z1}d_{1}} & e^{ik_{z1}d_{1}} & 0 & \cdots & 0 \\ -1 & -1 & e^{-ik_{z2}d_{2}} & e^{ik_{z2}d_{2}} & 0 & \cdots & 0 \\ \cdots & & & & \ddots & \\ 0 & 0 & \cdots & 0 & -1 & -1 & 1 \\ -\frac{k_{z1}}{\eta_{1}^{2}} e^{-ik_{z1}d_{1}} & \frac{k_{z1}}{\eta_{1}^{2}} e^{ik_{z1}d_{1}} & 0 & \cdots & 0 \\ \frac{k_{z1}}{\eta_{1}^{2}} & -\frac{k_{z1}}{\eta_{1}^{2}} & -\frac{k_{z2}}{\eta_{2}^{2}} e^{-ik_{z2}d_{2}} & \frac{k_{z2}}{\eta_{2}^{2}} e^{ik_{z2}d_{2}} & 0 & \cdots & 0 \\ \cdots & & & & & \\ 0 & 0 & \cdots & 0 & \frac{k_{zN}}{\eta_{N}^{2}} & -\frac{k_{zN}}{\eta_{N}^{2}} & \frac{k_{zN+1}}{\eta_{N+1}^{2}} \end{pmatrix} \end{cases}$$
(3)

Then the vectors  $B_2$  and C become

$$B_{2} = \begin{pmatrix} B_{1up} \\ B_{1down} \\ B_{2up} \\ \vdots \\ B_{N-1down} \\ B_{Nup} \\ B_{Ndown} \\ B_{N+1down} \end{pmatrix}, \qquad C = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ -\frac{k_{z0}}{\eta_{0}^{2}} \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$
(4)

This system will be overdetermined since there is one more equation than parameters to solve for. The overdetermined system can be solved by the least squares formula

$$B_2 = [A_2'A_2]^{-1}A_2'C$$
(5)

Thus, the field coefficients can be obtained for the p-polarized excitation light. This means that one can plot the electric field E against z within each material with

$$E_{z}(x, y) = -\frac{k_{xj}}{\eta_{j}^{2}} B_{jup} e^{i[k_{zj}[z-Zj]+k_{xj}x]} + \frac{k_{x}}{\eta_{j}^{2}} B_{jdown} e^{-i[k_{zj}[z-Zj]+k_{xj}x]}$$
(6)

$$E_{x}(x, y) = \frac{k_{zj}}{\eta_{j}^{2}} B_{jup} e^{i \left[k_{zj} \left[z - Zj\right] + k_{xj}x\right]} - \frac{k_{z}}{\eta_{j}^{2}} B_{jdown} e^{-i \left[k_{zj} \left[z - Zj\right] + k_{xj}x\right]}$$
(7)

Here Zj is simply the reference z coordinate at the interface of the (j-1)th and jth media.



Fig. S2 Reflectance spectra of the proposed biosensors with the configuration of HNTs/1L MoS<sub>2</sub>/3L BP/Au/prism. The refractive index of biosensing medium is set as  $n_s = 1.333$  RIU. The thickness of HNTs in (a) is 400 nm. The thickness of gold film in (b) is 40 nm.



**Fig. S3** (a) Reflectance spectra of biosensors proposed by us (solid lines, corresponding to the structure of 400 nm HNTs/1L MoS<sub>2</sub>/3L BP/40 nm Au/SF11 prism) and Ref. [25] (dashed lines, corresponding to the structure of 1L Graphene/4L BP/48 nm Au/100 nm BK7/SF11 prism). (b) Reflectance spectra of the biosensor configuration of 2L WSe<sub>2</sub>/5 nm BP/50 nm Ag/BK7 prism. The solid lines are calculated by considering the optical anisotropy and polarization dependent refractive index of BP. The dashed lines are calculated by using the fixed refractive index  $n_{BP} = 3.5 + 0.01i$  which is utilized by the authors in Ref. [23].



Fig. S4 (a) Variation of reflectance spectra with respect to the refractive index  $n_s$  of biosensing medium. (b) The change of phase difference  $\Delta \Phi_{\delta}$  and the change of SPR angle  $\Delta \theta_{SPR}$  at different refractive-index variates  $\Delta n$ . The refractive index of initial calibration biosensing medium is set as  $n_s = 1.333$  RIU.

## References

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