Supporting Information

4MBA-labeled Ag-nanorod aggregates by coated with SiO_2: synthesis, SERS activity, and biosensing application

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The immunoassay protocol

To visually describe the immunoassay protocol, the schematic representation of immunoassay protocol was plotted in Fig. S1. As shown in Fig. S1, the immune probe is firstly prepared by the chemical reduction process from Ag seed to Ag NRs with the help of CTAB; then, the as-prepared Ag NRs are labeled with 4MBA molecules; subsequently, the silica shell is successfully coated on the surface of Ag NRs aggregate to form 4MBA-Ag NRs@SiO_2, and the anti-PSA antibody is immobilized on the surface of silica. Meanwhile, the immune substrate is fabricated by immobilizing Ag NRs on the quartz slide and anti-PSA antibody on the surface of Ag NRs and the naked surface of substrate is blocked by BSA. Finally, a sandwich structure is consisted of the immune probe, PSA and the immune substrate. After going through a series of washing step, the sandwich structure was tested by using Raman spectrometer to obtain the SERS spectra of 4MBA with different concentrations of PSA.

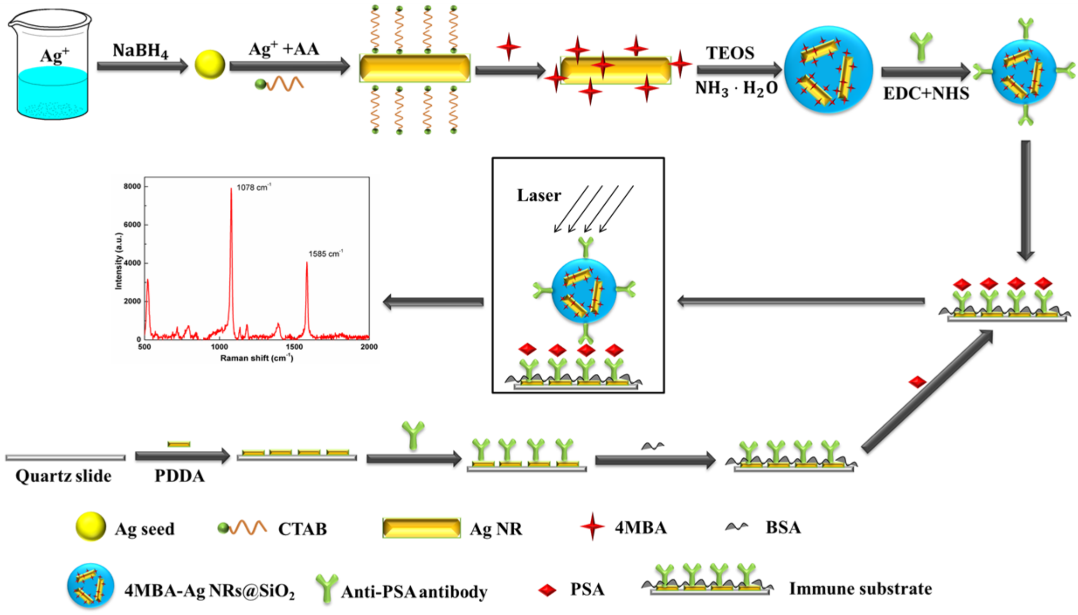

Fig. S1 Schematic representation of the immunoassay protocol

High sensitive immunoassay

According to the immunoassay protocol described in this paper, the immunoassay experiments have been performed for different PSA concentrations. In Tab. S1, the experimental results including the standard error and the confidence intervals (α=0.05) were provided. It can be seen that the SERS intensity of 4MBA at 1078 cm^{-1} have a significant decrease with the decreasing concentration of PSA and the limit of detection of PSA arrived 0.3 $fg \cdot ml^{-1}$ (8.824×10^{-18} mol/L).

Tab. S1 Statistic data for peak intensity at 1078 cm^{-1} with different concentrations of PSA

Concentration of PSA	Intensity of peak at 1078 cm^{-1}	Standard error	Confidence intervals	
			Lower limit	Upper limit
3 $\mu g \cdot ml^{-1}$	17521.51	2681.86836	15311.79392	25296.16808
30 $ng \cdot ml^{-1}$	13441.62	532.0856	12671.861	14264.199
0.3 $ng \cdot ml^{-1}$	11111.6986	1338.693	9966.899	13285.761
3 $pg \cdot ml^{-1}$	6936.79252	1456.65826	5808.286447	7913.945553
30 $fg \cdot ml^{-1}$	2535.514	417.6668	2326.1022	2843.8378
3 $fg \cdot ml^{-1}$	1538.49048	176.5036	1242.2519	1641.0441
0.3 $fg \cdot ml^{-1}$	1067.04695	81.43581	1093.0934863	1194.0405137

SERS active of the samples

In order to verify the reliability of SERS measurements, the repetitive experiments were carried out for three types of 4MBA-Ag NRs@SiO_2 samples (Type I, II and III) and the results were shown in Fig. S2. Each type of samples were consisted of 5 samples and prepared with the conditions of 0.02, 0.05 and 0.08 M CTAB, respectively. As shown in Fig. S2, the SERS spectra of each type of samples are almost same in 5 independent measurements, but there are considerable differences in their intensity of SERS signals for the different type of samples. It can be seen that, comparing Fig. S2(b) with Fig. S2(a) and (c), the second type of samples exhibit a stronger SERS signal, which is consistent with their EF values calculated by using Eq. 1 in this paper. It can be concluded that the as-synthesized 4MBA-Ag NRs@SiO_2 exhibits excellent SERS performance with a good repeatability.

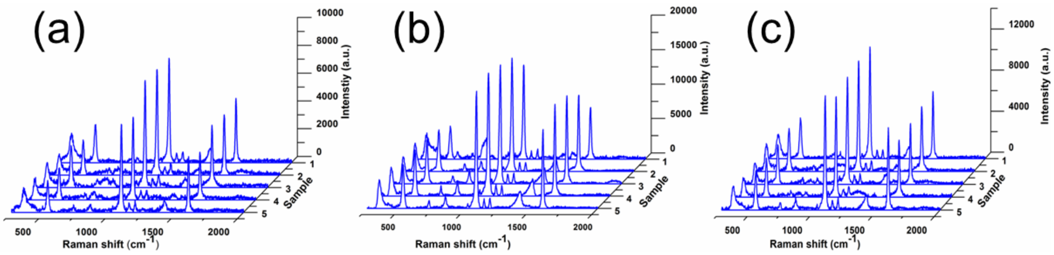

Fig. S2 SERS spectra of three types of 4MBA-Ag NRs@SiO_2 samples.

(a) Type I, (b) Type II, and (c) Type III