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Recyclable Tetracycline Imprinted Polymeric SPR Sensor: in Synergy with Itaconic acid and Methacrylic acid

Tehseen Nawaz^a, Muhammad Ahmad^c, Jieying Yu^b, Shiqi Wang^b and Tianxin Wei,*^b

^{a.} Department of Chemistry, The University of Hong Kong, Hong Kong. Email: u3007040@connect.hku.hk

^b Key laboratory of Cluster Science of Ministry of Education, Beijing Institute of Technology, Beijing 100081, China. Email: txwei@bit.edu.cn

^c Department of Mechanical engineering, City University Hong Kong, Hong Kong.

Supplementary Materials

Successful formation of (IA-MAA@SPR) MIPs sensor chip was analyzed by Fig. S1 (A), giving the real time kinetic curve for the polymerization. First, the film was grafted on modified gold-plated chip by utilizing RAFT polymerization in visible light which was indicated by coupling angle shift from 58° to 68° (see Fig. S1B.). Then the film was rinsed with washing solution for 20 min which resulted in the removal of template molecules and the reflectivity value decreased with time as shown in Fig. S1 (B).



Fig. S1. (A) Polymerization of (IA-MAA@SPR)MIPs sensor chip and (B) Washing of template molecules

Real time monitoring of (IA-MAA@SPR)MIPs sensor chip was done by SPR to investigate the specificity of sensor. Rebinding curve of TC exhibited maximum variation in reflectivity while treating with IA-MAA@SPR sensor chip (Fig. S2. a). On the other hand OTC, CTC and CAP presented negligible response (see Fig. S3. b, c & d). Hence this specific behavior indicated the presence of highly selective tetracycline-imprinted recognition sites.

The angular reflectivity spectroscopy was fitted by Transfer Mixed Based Model which was implemented in Winspall software. The parameters are as follows:

The refractive index of prism $n_p = 1.845$, thickness $d_m = 45$ nm and refractive index for gold film $n_m = 0.3507 + 3.2805$ and refractive index of buffer $n_b = 1.336$ The surface coverage of sensor chip can be estimated by applying following equation 1.

$\Gamma = (n_f - n_b) d_f \partial c / \partial n \dots (1)$

Where n_b and n_f are the refractive index of adsorption solution and the MIPs SPR sensor chip respectively. D_f is the thickness of template Imprinted film. The factor $\partial c/\partial n = 0.2 \text{mm}^3/\text{mg}$ that varies with the concentration of absorption solution. By implication of fitting spectra, the thickness and refractive index of MIPs were calculated as $d_f = 481 \text{ nm}$ and nf = 1.4212, respectively. Accordingly, the mass coverage of MIPs on the gold substrate was determined as $\Gamma = 205.6 \text{ ng/mm}^2$ according to given equation which decreased to 10.8 ng/mm² after washing (1).



Fig. S2. (A) Response of SPR for absorption of: (a) TC, (b) OTC, (c) CTC and (d) CAP (each at 10⁻⁹ mol/L)



Fig. S3. Recoverability of (IA-MAA@SPR)MIPs sensor chip for adsorption of 10-9 mol/L TC in PBS at pH = 7.4

To ensure the stability of prepared sensor, the (IA-MAA@SPR)MIPs sensor chips were stored at room temperature for 30 and 60 days. After storage, the same chip was implied for detection of tetracycline in sample solution. The real time monitoring in SPR is shown in Fig. S4. Expectedly, the sensor chip displayed high degree of stability and retained its efficiency by 89.14% and 80.73%, respectively.



Fig. S4. The rebinding kinetics of TC (10-9 mol/L) in PBS buffer solution after 0, 30 and 60 days at room temperature

1. Wang Y, Huang C-J, Jonas U, Wei T, Dostalek J, Knoll W. Biosensor based on hydrogel optical waveguide spectroscopy. Biosensors and Bioelectronics. 2010;25(7):1663-8.