Supplementary Information (SI) for Analyst.
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Supplemental material

Electrochemical immunosensor based on MXene-Au and Au-Ce-COF for detection of methyl parathion

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1. Experimental section

1.1. Reagents and apparatus

phoxim (PHO), malathion-d6 (MLT-d6), dimethoate (DMT), Bovine serum albumin (BSA), hydrofluoric acid (HF), methylene blue (MB), chloroauric acid ($HAuCl_4$), Potassium chloride (KCl), 2,4,6-Trihydroxy-benzene-1,3,5-tricarbaldehyde (TFP, $C_9H_6O_6$), 4,4',4''-(1,3,5-Triazine-2,4,6-triyl)trianiline (TAPT, $C_{21}H_{18}N_6$), Cerium nitrate hexahydrate ($Ce(NO_3)_2 \cdot 6H_2O$) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Trichlorfon (TF), and chlorpyrifos (CPF) were purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). Potassium ferricyanide ($K_3[Fe(CN)_6]$), Sodium phosphate dibasic dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), Sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$), Sodium chloride (NaCl), Ethanol (C_2H_6O), N,N-Dimethylformamide (DMF, C_3H_7NO) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ti_3AlC_2 powder (MAX) was purchased from Shanghai Haohong Bio-pharmaceutical Technology Co Ltd. (Shanghai, China). All chemicals were of analytical grade and used without further purification.

Antigen (ATG: parathion-methyl-BSA conjugate) and antibody (Ab: anti-parathion-methyl) were provided by Landu Bio-technique (Shandong, China).

Electrochemical analysis was done on electrochemical workstation (CHI660D, Shanghai, China). A three-electrode system was used in this experiment, including a modified glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode and an $Hg/HgCl_2$ reference electrode (saturated KCl solution). The morphology and structure observations were performed on scanning electron microscope (SEM, Hitachi S-4700 II, Japan) and transmission electron microscope (TEM, FEI Tecnai G220, American). X-ray diffraction (XRD, Panalytical, The Netherlands) scanning from 3° to 80° at a scan rate of 2° minute $^{-1}$ using quartz monochromatic Cu Kα1 radiation source (λ = 0.1541 nm). Fourier transformation infrared spectra (FT-IR, Bruker ALPHA, German) were recorded to determine the chemical structure of the compounds. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, American) spectra were recorded by a Physical Electronics PHI 5000 Versa probe spectrometer with Al Kα radiation (1468 eV). Ultraviolet-Visible Spectroscopy (UV-2600, shimadzu, Japan) recorded UV-Vis diffuse reflectance spectra in the range of 450 - 800 nm.

1.2. Synthesis of MXene-Au-MB-ATG as signal probe

MXene-Au was synthesized according to the reported methods with modifications.[1] For MXene synthesis, 150 mg of Ti_3AlC_2 powder was slowly added to 30 mL of hydrofluoric acid (HF, 40%) and stirred continuously for 48 h at room temperature to ensure that the aluminum was etched out of the solid. Then, it was washed and centrifuged (8000 rpm, 5min) several times with ultrapure water until the pH of the product reached 6.0. The solid product was then vacuum dried at 60°C for 12 h to yield MXene powder.

MXene-Au was synthesized through the in situ reduction reaction. First, 100 mg of MXene was dispersed in 20 mL of ultrapure water and sonicated for 20 minutes. Under stirring conditions, 5 mL of $HAuCl_4$ (20 mM) was then added to the MXene dispersion to grow AuNPs in situ. The product was centrifuged three times (8000 rpm, 5 min) to obtain MXene-Au powder. Then, 5 mg of MXene-Au composite was added to 400 μA of methyl bromide (0.05 mM) and sonicated for 30 min. Methyl bromide molecules were adsorbed onto MXene-Au through electrostatic adsorption to form the

MXene-Au-MB complex. The product was centrifuged (3000 rpm, 5 min) to remove excess MB molecules from the supernatant and re-dispersed in 2 mL deionized water. Finanly, incubate 2 mL of MXene-Au-MB and 1 mL of ATG (8 μg/mL) with continuous shaking for 2 h at 37°C. The AuNPs were efficiently captured by ATG through the Au-N bond. After wash with 0.01 M phosphate buffer (PBS) centrifugation (1500 rpm, 10 min), the resulting MXene-Au-MB-ATG was dissoloved in 2 mL deionized water and stored at 4°C for further use.

1.3. Preparation of Au-Ce-COF composite

The COF nanoparticles were synthesized according to the reported method.[2] 355 mg of TAPT and 210 mg of TFP were added to a three-necked flask, and 20 mL of anhydrous DMF was added with continuous stirring. The solution was then refluxed under nitrogen atmosphere for 12 h. The product was then washed with DMF and anhydrous ethanol alternately for several times, and dried at 60°C under vacuum environment for 12 h until the yellow COF powder was obtained. Dissolve 70 mg of the above synthesized COF and 70 mg of $Ce(NO_3)_2 \cdot 6H_2O$ into 25mL of anhydrous ethanol using in a round bottom flask, and then reflux under nitrogen atmosphere for 24 h with continue stirring. The product washed with ethanol for many times, and dried under vacuum at 80°C for 12 h to get the yellowish orange Ce-COF powder.

The Au nanoparticles were synthesized with the traditional trisodium citrate reduction route.[3] In a beaker, 1 mL of 20 mM $HAuCl_4$ was diluted with 30 mL of ultrapure water and heated to boiling with continuous stirring. After that, 2 mL of 1% (wt%) trisodium citrate was added, and the solution was maintained boiling and stirring for 20 min. The product was cooled down to room temperature to obtain the burgundy colored nano-gold gel and stored at 4°C.

20 mg of Ce-COF powder was dissolved in 10 mL of ultrapure water and ultrasonicated for 10 min. 5 mL of gold nanogel was then added into Ce-COF dispersion and continued to be ultrasonicated for 20 min to prepare Au-Ce-COF.

1.4. Fabrication of electrochemical immunsensor

To fabricate the electrochemical immunosensor, the bare GCE was first carefully polished with 0.05, 0.3 and 1 μm Al_2O_3 powders to obtain a mirror-like surface. Next,

2 mg of Au-Ce-COF was completely dissolved in ultrapure water and 10 μL of Au-Ce-COF was added dropwise onto the surface of the pre-treated GCE. After drought at room temperature, 10 μL of 8 μg/mL Ab was placed on Au-Ce-COF/GCE and incubated at room temperature for 120 min to immobilize Ab on the electrode surface. The electrode surface was washed three times with 0.01 M PBS to remove weakly bound or unbound Ab. Then, 5 μL of 1% (wt%) BSA solution was added dropwise and incubated at room temperature for 30 min to block the non-specific binding site, and then the electrode surface was washed three times with 0.01 M PBS to remove the excess BSA. Finally, 10 μL of different concentrations of MXene-Au-MB-PTM was added dropwise and incubated for 120 min to achieve the detection of the target.

Reference

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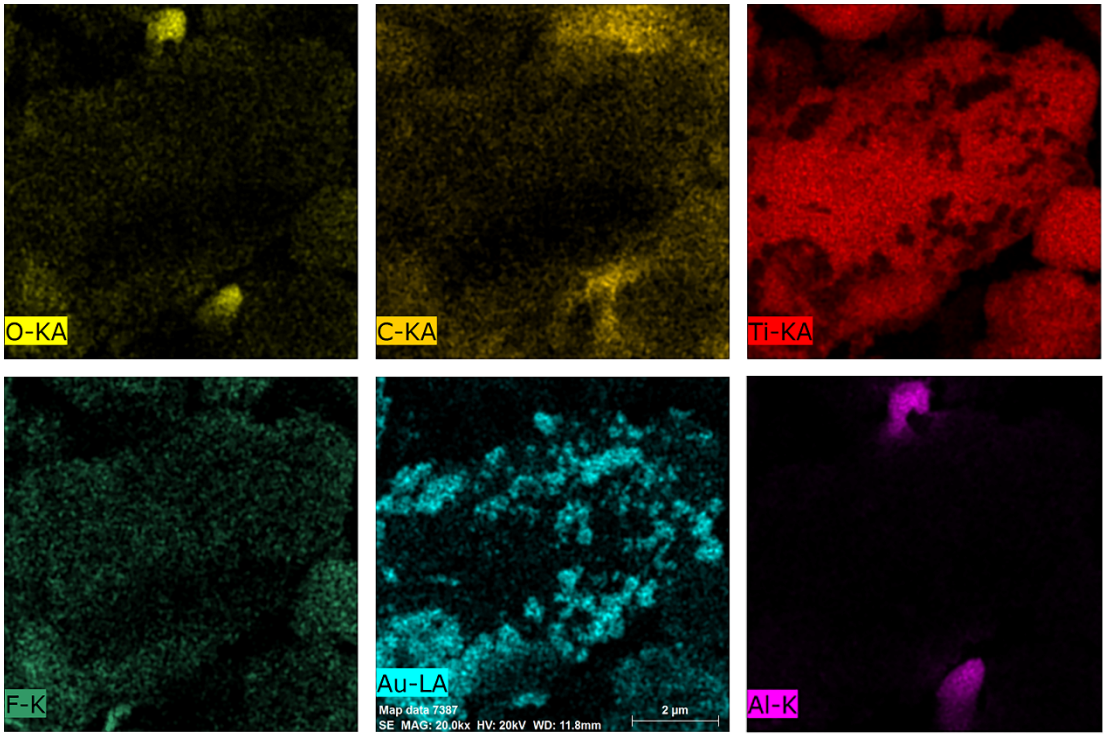

Fig. S1. SEM and mapping images of MXene-Au.

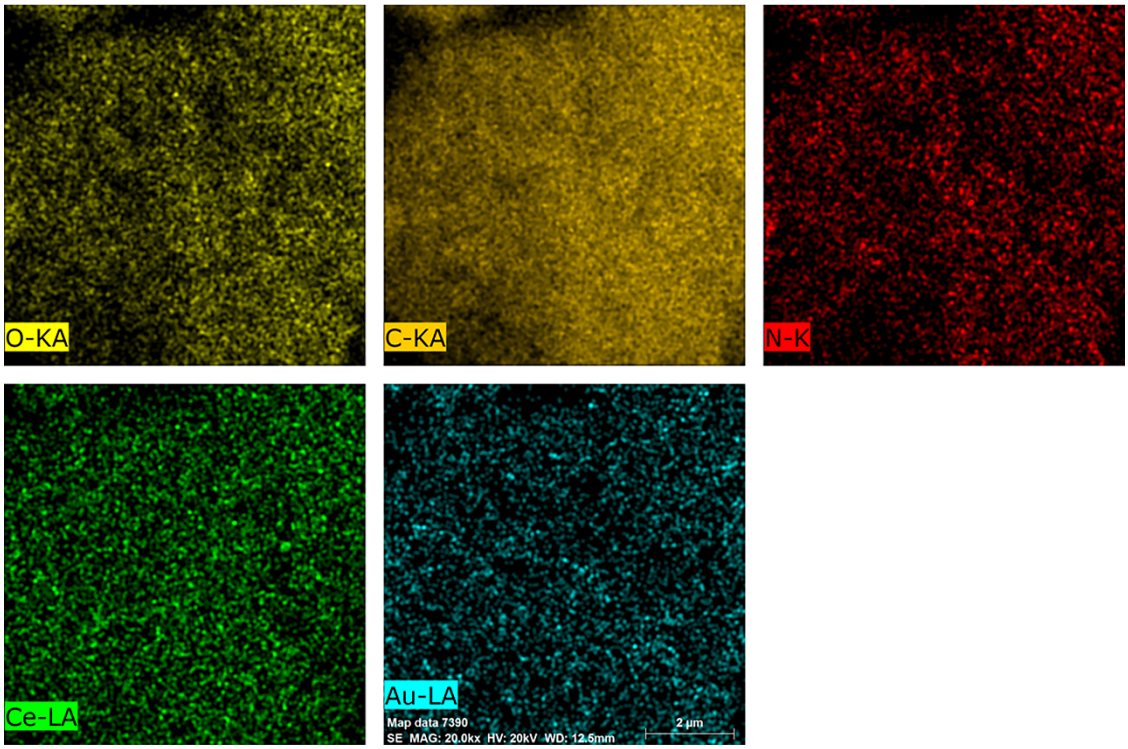

Fig. S2. SEM and mapping images of Au-Ce-COF