

Supplemental Information

Visible light photoelectrochemical sensor based on Au nanoparticles and molecularly imprinted poly(o-phenylenediamine) modified TiO₂ nanotubes for specific and sensitive detection chlorpyrifos

Panpan Wang, Weijian Dai, Lei Ge, Mei Yan, Shenguang Ge, Jinghua Yu*

Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, P.R. China

Preparation of TiO₂ NTs

The Ti foil (0.1 mm thickness, 99.6 % purity, Goodfellow, England) was cleaned by using distilled water and acetone and dried off with N₂ gas. The bare Ti foil was anodized in an ethylene glycol solution containing NH₄F (0.38 wt%) and H₂O (1.79 wt%) and placed in a well-insulated bath for 3 h at 30 V and at 20 °C using a dc power supply (N5753A model, Agilent). The textured Ti surface was obtained by removing the first anodized TiO₂ nanotubular layer with an adhesion tape. Subsequently, the second anodization was performed for 5 min under conditions identical to those in the first anodization step. After the second anodization step, the sample was washed with distilled water and acetone and then dried off with N₂ gas. The as-formed TiO₂ NTs have an amorphous structure but the phase can be converted into anatase or rutile through annealing. Thus, thermal annealing of the anodized TiO₂ NTs was carried out 500 °C for 2 h with

a heating and cooling rate of 1.7 °C/min in an ambient condition.

Electrochemical impedance analysis

Electrochemical impedance spectra (EIS) were performed to provide further evidence of interface properties and to study the electrical behaviors of the layers composing the interface. EIS were carried out in a background solution of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ PBS. The frequency range was 100 MHz to 10 KHz. At higher frequency, the semicircle controls the interfacial electron-transfer rate of the redox-probe between the solution and the electrode, and can be used to describe the interface property of the electrode (Sallacan et al., 2002). In EIS, the diameter of the semicircle at higher frequencies corresponds to the electron-transfer resistance (R_{et}); a change in the value of R_{et} is associated with the blocking behavior of the modification processes on the electrode surface, and is reflected in the EIS as a change in the diameter of the semicircle at high frequencies.

Herein, the electron-transfer of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ onto the surface of TiO_2 NTs were blocked by the formation of PoPD-AuNPs on the surface of TiO_2 NTs, which resulted in an increase in R_{et} . Figure 6 shows the EIS of TiO_2 NTs at different stages of treatment. The EIS of bare TiO_2 NTs showed a relatively small R_{et} value (Figure S1, curve a). After modification with AuNPs, EIS showed a decrease in R_{et} (curve b), which may be because the presence of AuNPs can provide a conductive pathway to electron transfer and promote electron transfer reactions of $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The R_{et} increased remarkably upon the formation of the chlorpyrifos-PoPD film (curve c). This result indicates PoPD film have the larger obstruction effect, which results in reducing electron transfer rate or increasing resistance to the flow of electrons. However, after removal of chlorpyrifos, the impedance (curve d) decreased accordingly. The reason may be that removal of

chlorpyrifos left a lot of cavities in PoPD film, and reduced the mass-transfer resistance of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ through PoPD film, and as a result accelerated the electron-transfer between the electrolyte and electrode surface. This phenomenon was consistent with literature (Xie et al., 2010).

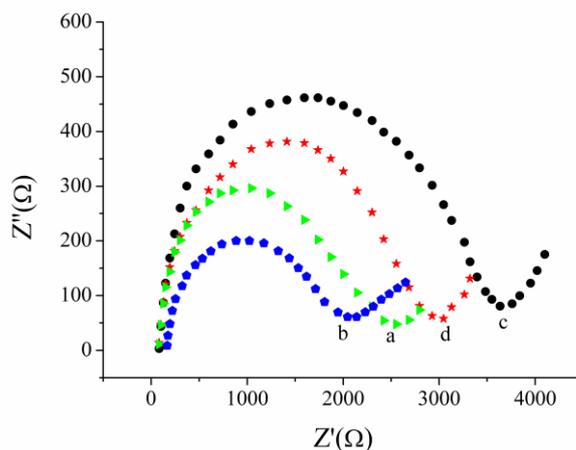


Figure S1. Electrochemical impedance spectra in 0.1 M KCl containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. (a) Bare TiO_2 NTs; (b) AuNPs/ TiO_2 NTs; (c) Chlorpyrifos-PoPD-AuNPs/ TiO_2 NTs (d) PoPD-AuNPs/ TiO_2 NTs.

PEC detection of chlorpyrifos

The limit of detection is calculated at the concentrations which produced three times $\text{PEC}_{\text{blank}}$ (signal-to-noise (S/N) = 3, n=10). As shown in Table. S1, the chlorpyrifos solution of 0.96 $\text{nmol}\cdot\text{L}^{-1}$ produced three times $\text{PEC}_{\text{blank}}$. Consequently, the limit of detection was calculated as 0.96 $\text{nmol}\cdot\text{L}^{-1}$.

Table S1 The calculation of detection limit.

| $C_{\text{chlorpyrifos}} / \text{nmol}\cdot\text{L}^{-1}$ | Photocurrent $/(10^{-7}\text{A})$. (n=10) | Average | S/N |
|---|---|---------|------|
| 0 | 0.9, 0.8, 1.0, 1.1, 0.9, 1.0, 0.9, 0.9, 1.0, 1.1 | 0.96 | 3.01 |
| 0.96 | 2.8, 2.9, 3.0, 2.7, 2.9, 2.8, 2.8, 2.9, 3.1, 3.0, | 2.89 | |

Selectivity of the PEC sensor

The selectivity was evaluated by calculating the photocurrent ratio (PI/PI0), where PI and PI0 were photocurrent which were recorded in 0.1 M PBS (pH=6.86) after the incubation of PoPD-AuNPs/TiO₂ NTs in chlorpyrifos solution in the presence (PI) and absence (PI0) of interferences. Results showed that 20-fold atrazine, paraquat, and acetamiprid hardly caused significant change of the photocurrent of chlorpyrifos, where the photocurrent increased only 2.0%, 1.5% and 0.5%, respectively (Figure S2). 100-fold oxygen-containing inorganic ions (SO₄²⁻, PO₄³⁻) and 50-fold metal ions (Ca²⁺, Mg²⁺) had tiny influence on the determination of chlorpyrifos, where the photocurrent increased only 0.9%, 0.6%, 0.5%, 0.7%, respectively. This phenomenon can be attributed to the application of molecular imprinting technique. It can be explained as that recognition sites formed in PoPD film could distinguish chlorpyrifos from other species through molecular size and functionalized group distribution, and rebind chlorpyrifos selectively by hydrogen bonds interaction. Then chlorpyrifos was specifically accumulated on the surface of the PEC sensor, whereas other coexistent molecules and ions not complementary to the recognition sites and remained in the bulk solution. After washing with distilled water, chlorpyrifos stay on the PoPD-AuNPs/TiO₂ NTs, but the interferences were removed for the nonspecific adsorption. This kind of selectivity was even more specific than that of the enzyme inhibition bioelectrochemical sensor (Kim et al., 2008).

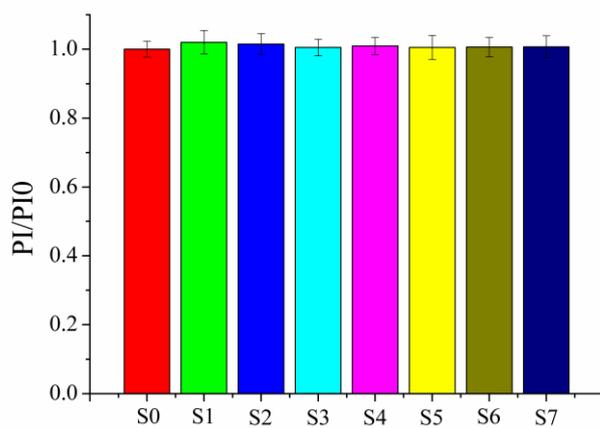


Figure S2. Photocurrent ration of the PoPD-AuNPs/TiO₂ NTs in 0.1 M PBS (pH 6.86) after incubated in 1 $\mu\text{mol}\cdot\text{L}^{-1}$ chlorpyrifos in the absence (PI0) and presence (PI) of atrazine (S1), paraquat (S2), acetamiprid (S3), SO₄²⁻ (S4), PO₄³⁻ (S5), Ca²⁺ (S6) and Mg²⁺ (S7) respectively.

References

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