

Supporting Information

Electropolymerized Molecularly Imprinted Polypyrrole Film for Dimethoate Sensing: Investigation on Template Removal after the Imprinting Process

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Materials and methods

Chemicals and materials

Pyrrrole (98%, Sigma-Aldrich) was purified by vacuum distillation, the boiling point was reached at 95 ° C and the colorless liquid obtained was kept in the dark at -20 ° C until its use. Dimethoate (≥98%, PESTANAL®, analytical standard, Merck), was stored at + 4°C until its use. Gold foils (0.5 mm thick, 99.95% metals basis, Alfa Aesar, Germany) were cleaned following a specific procedure. All experiments were carried out in Milli-Q water (18.2 MΩ·cm, Millipore, Bedford, MA, USA). The experimental apparatus used in this work for all measurements is based on three-electrode system: a pure gold foil as working electrode, a platinum foil as counter electrode and an Ag/AgCl/KCl sat. as reference electrode, made in laboratory and having a potential of 103 mV with respect to the SCE (saturated calomel electrode). All potentials reported in the present paper are referred to the aforementioned reference electrode. All cyclic voltammetry analyses were carried out using PARSTAT® 4000 potentiostat-galvanostat-impedance analyzer, controlled by VersaStudio software. Instead, square wave voltammetry analyses were performed with CH Instruments potentiostat, model 1230B. X-ray photoelectronic spectroscopy analyzes were carried out with Versa Probe II Scanning XPS (Physical Electronics GmbH) spectrometer and an AlK α source having a 200

μm spot. All wide-scan and high-resolution spectra were obtained in FAT mode with step energy of 117.40 eV and 29.35 eV, respectively, and with source power of 49.2 W. The charge compensation was performed with an electronic cannon operating at 1.0 V and 20.0 μA . The data were analyzed with the MultiPak v. 9.9.0.8 software.

Synthesis of MIP and non-molecularly imprinted polymer (NIP) and electrochemical measurements

The bare gold electrode (AuE) was immersed in piranha solution for 15 minutes, in order to allow organic matter removal from its surface, rinsed with water and polished with Acetone (ACS Reagent). Alumina powder was used for the mechanical electrode polishing, followed by sonication for 4 minutes at room temperature. Then, an electrochemical cleaning by cyclic voltammetry (CV) was performed using H_2SO_4 solution 0.5 M in the potential range between -0.3 and +1.7 V at a scan rate of 300 mV s^{-1} .^[1] AuE was immersed in phosphate buffer (PB, pH = 6.8, 0.1M) containing 30 mM of Pyrrole (Py) and 10mM of Dimethoate (DMT) for the electropolymerization of MIP by CV in the potential range between -0.4 V and +1.5 V, in accordance with the IUPAC bias where oxidation currents have positive values, at a scan rate of 50 mV s^{-1} . Considering the influence of the number of cycles on the thickness of the polymer, an optimal value of 10 cycles was selected.^[2,3] Electrochemical deposition was followed by analyte removal from the polymer just imprinted by experimenting three washing methods such as 0.01M HCl, 0.1M HCl and 0.1M NaOH. During this step, AuE was immersed in these different solutions and kept under constant stirring by using a magnetic stirrer for 30 minutes at room temperature. Washing times extended to 45 minutes were also tested for the HCl solution. Finally, for the rebinding step, the MIP sample was dipped for 15 minutes in solutions with different concentrations of dimethoate in PB, namely 2, 4 and 100 pM. After rebinding, the foils were washed with Milli Q water and dried under a nitrogen flow (Figure S1). A control electrode, “non-molecularly imprinted polymer” (NIP), was prepared under the same conditions but with no dimethoate during the electropolymerization.

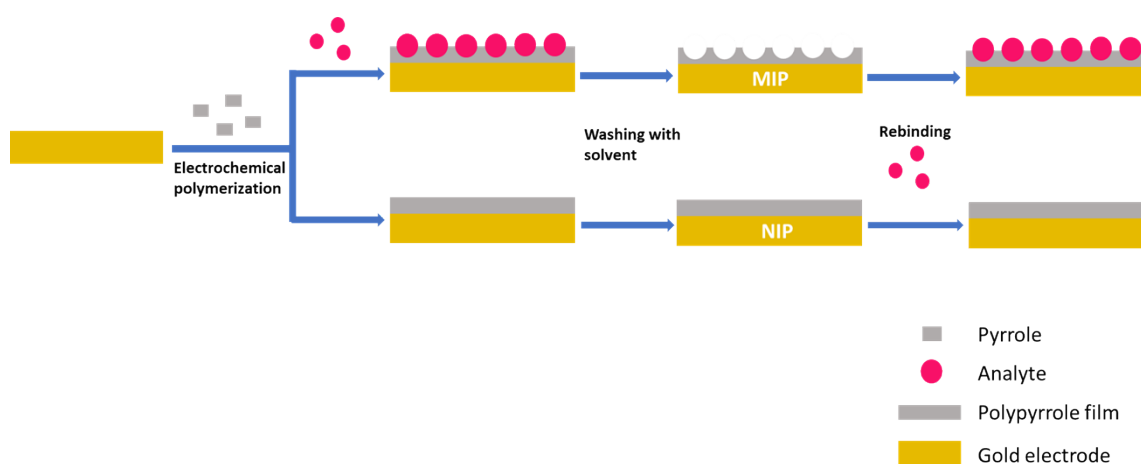


Figure S1. Schematic representation of imprinting process. The analyte molecules interact with monomers, favoring the polymerization around the species, and the template is subsequently removed by solvent extraction, creating cavities that have a permanent memory for rebinding.

Electrochemical measurements were carried out with CV on NIP and MIP before and after molecular imprinting removal, using PB containing 5 mM of $K_4[Fe(CN)_6] \cdot 3H_2O$, 5 mM of $K_3[Fe(CN)_6]$ and 0.1 M of $NaNO_3$ (support electrolyte), applying a potential range from -0.3 V to +0.8 V at a scan rate of 10 mV s^{-1} , for 3 cycles; a control CV was also performed on bare AuE without polypyrrole (PPy), under the same conditions. These operations have been repeated three times, to evaluate their reproducibility.

Square wave voltammetry (SWV) analyzes were performed in a potential range between 0 and +0.6 V, frequency of 5 Hz and amplitude of 0.01V, always using the same solution of $K_4[Fe(CN)_6] \cdot 3H_2O$, $K_3[Fe(CN)_6]$ and 0.1 M $NaNO_3$ in PB as probe.

Results and discussion

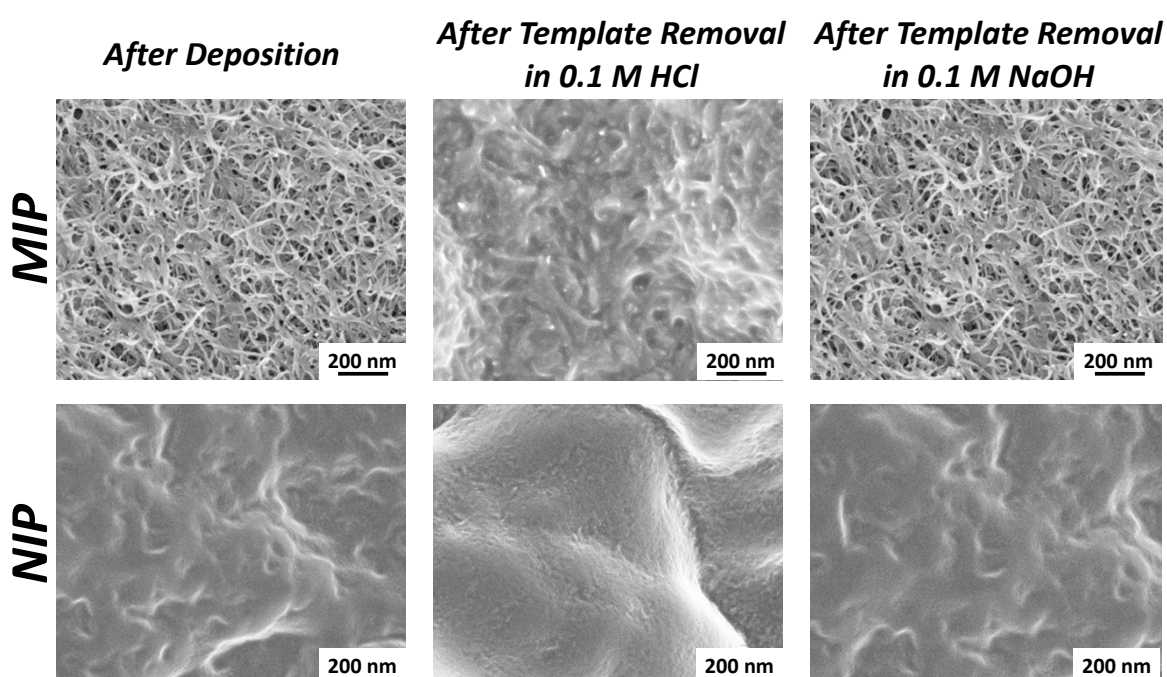


Figure S2. SEM pictures for PPy-MIP and PPy-NIP modified electrodes after deposition, after 0.1M HCl template removal protocol and after 0.1M NaOH template removal protocol.

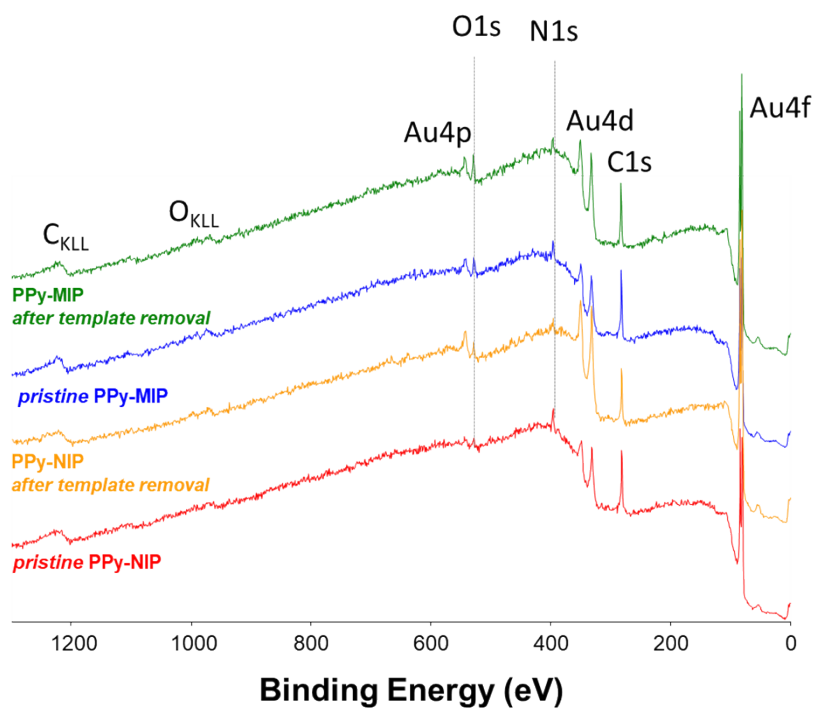


Figure S3. Wide-scan XPS spectrum of PPy-NIP and PPy-MIP before and after template removal protocol.

Table S1. The table shows PPY-NIP signals with relative chemical assignment. The values are expressed as average values $\pm 1\sigma$ ($n = 3$).

<i>NIP</i>		<i>BE / eV</i>	<i>Chemical assignment</i>
		397.8 ± 0.2	<i>C=N</i>
<i>N1s</i>		399.7 ± 0.2	<i>NH</i>
		401.9 ± 0.2	<i>C-N⁺</i>
		283.9 ± 0.2	<i>C_β</i>
		284.7 ± 0.1	<i>C_α</i>
<i>C1s</i>		285.8 ± 0.2	<i>C-OH, C=N, C-N⁺</i>
		287.4 ± 0.2	<i>C=O</i>
		288.7 ± 0.2	<i>COOH, COO⁻</i>
		529.3 ± 0.2	<i>Inorganic O</i>
<i>O1s</i>		530.9 ± 0.2	<i>C=O, COO⁻</i>
		532.6 ± 0.2	<i>C-OH</i>

Table S2. The table shows PPY-MIP signals with relative chemical assignment. The values are expressed as average values $\pm 1\sigma$ ($n = 3$).

<i>MIP</i>		<i>BE / eV</i>	<i>Chemical assignment</i>
		398.1 ± 0.2	<i>C=N</i>
<i>N1s</i>		399.8 ± 0.2	<i>NH</i>
		401.4 ± 0.2	<i>C-N⁺</i>
		283.9 ± 0.2	<i>C_β</i>
		284.8 ± 0.2	<i>C_α</i>
<i>C1s</i>		285.8 ± 0.2	<i>C-OH, C=N, C-N⁺</i>
		287.4 ± 0.2	<i>C=O</i>
		288.7 ± 0.2	<i>COOH, COO⁻</i>
<i>O1s</i>		531.5 ± 0.2	<i>C=O, COO⁻</i>
		532.6 ± 0.3	<i>C-OH</i>

References

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