Improving self-supported nanowire arrays by response surface methodology*

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Introduction

Nanostructured sensors are a promising high-sensitive alternative for H_2O_2 detection [2, 1]. However, nanostructuring increases the number of variables influencing the sensor's behavior, which raises the problem of choosing the best combination of variables and their levels to increase the sensor's sensitivity.

The Response Surface Methodology (RSM) is a principled approach that has proved to be efficient in terms of the necessary steps to find the best subset of variable levels while considering possible interaction between factor levels.

Here we applied the RSM to optimize a Nickel (Ni) sensor response to H_2O_2 , fabricated using electrodeposition in nanoporous membranes of Polycarbonate (PCTE). As design variables, we used the length of the nanowire, the measuring potential, and H_2O_2 concentrations.

Our self-supported nanowire array sensor achieved better results compared to a planar and other nanostructured sensors.

RSM

The **RSM** is a process (Fig. 1**b**). The first step in this process is to start with a simple design, like a 2^k augmented with n_c center points (Fig. 1**a** illustrate the a 2^2), to fit a first order model (FOM) of the form $y = \beta_0 + \sum_i^k \beta_i x_i + \varepsilon$, for k factors, and normally-distributed error ε. The $x \in [-1, 1]$ are *coded variables* centered at 0.

The next step is to move in the direction of improvement by using the partial regression coefficients β_i. New values of x_k factors are found with the relation $\Delta x_i = \frac{\beta_i}{\beta_j} \Delta x_j$, by choosing as β_j the largest effect [4].

When quadratic effects are detected (e.g., with a lack-of-fit and a curvature test), the 2^k design is augmented with 2 axial points by factor choosing levels at α distance of the center. The new design is now called Circumscribed Central Composite (CCC) design [4]. This design is suitable to fit a second-order model (SOM).

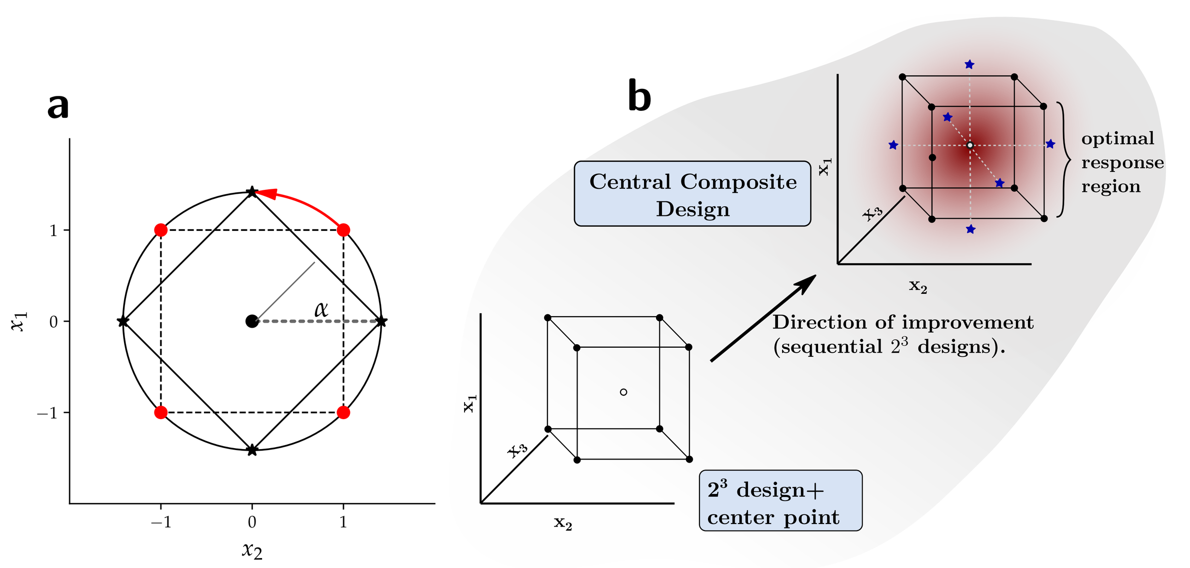

Fig. 1: RSM process

$$y = \beta_0 + \sum_i^k \beta_i x_i + \sum_{ii} \beta_{ii} x_i^2 + \sum_{i<j}\sum \beta_{ij} x_i x_j \quad (1)$$

With a SOM we can approximate concave functions to surfaces and optimize for factor levels at which the system response is maximum (Fig. 1**b**).

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Method

We started with a 2^3 design (Fig. 1**b**), with H_2O_2 concentrations of 1.27 and 3.81 mM (low and high), lengths of 1.3 and 3 μm, and potential of -0.05 and 0.05 V. Four center points runs were added with 2.54 mM, 2.15 μm and 0 V. For the CCC design, que added axial points at $\alpha = \sqrt{3} = \pm 1.73$. In natural variables, for length 0.68 and 3.62 μm; H_2O_2 concentration of 0.34 and 4.74 mM, and for potential -0.0867 and 0.0867 V.

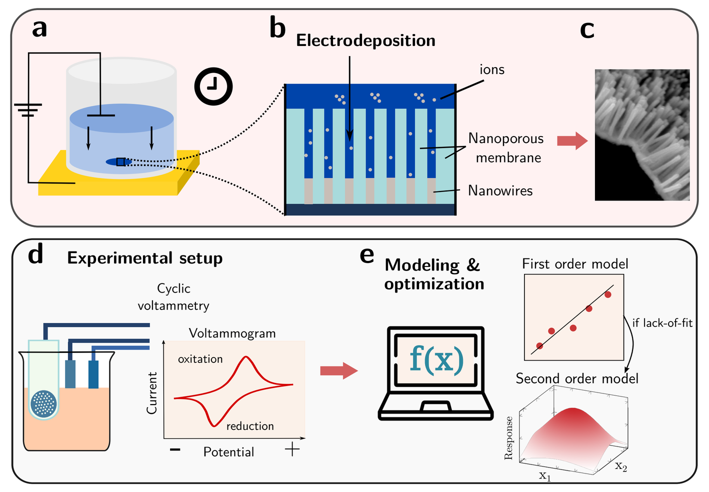

Fig. 2: Electrode fabrication and experimental setup

The desired nanowire length was achieved by monitoring the time of electrodeposition of Ni ions using PCTE restrictive nanoporous membranes with a pore size of 0.1 μm and 0.6 μ thickness. Lengths were measured using scanning electron microscope (SEM; see Figure 2 **a**-**c**).

Sensor responses were measured using Cyclic voltammetry (CV) with a scan rate of 100 mVps, with a range of -0.6, 0.6 V.

Results

2^k and FOM. All the coefficients were non-significant in the FOM, but the lack-of-fit ($F(5, 3) = 18.27$, $p < 0.05$) and curvature ($F(1, 3) = 66.71$, $p < 0.01$) both were significant, suggesting quadratic effects (see Fig. 3).

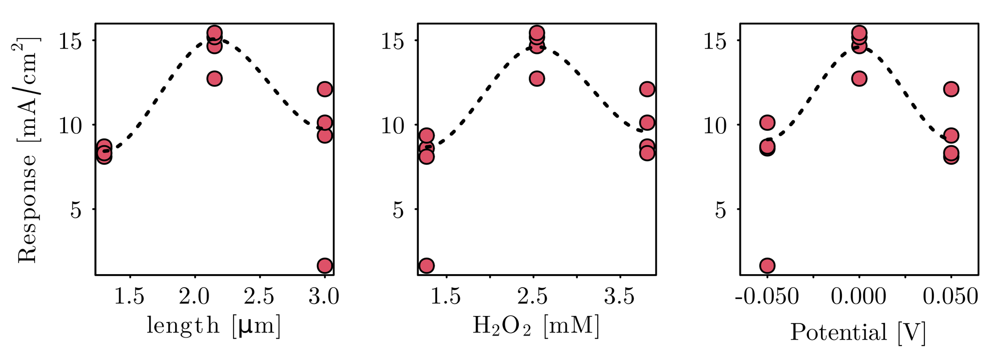

Fig. 3: Quadratic response. The line shows a fitted LOESS.

		Estimate	$t(14)$
Main effects	β_1	0.22	0.50
	β_2	0.83	1.92
	β_3	2.10	6.60*
Interaction terms	β_{12}	1.36	2.38*
	β_{13}	1.32	2.31*
	β_{23}	-0.70	-1.23
Quadratic terms	β_{11}	-1.24	-3.15*
	β_{22}	-1.23	-3.11*
	β_{33}	-3.61	-10.29*

Tab. 1: Statistics of the second-order model. *: $p < 0.05$

CCC and SOM. The main effects Length and H_2O_2 Concentration were non-significant, Potential was significant. The interactions Length × Concentration and Length × Potential also were non-significant, but Concentration × Potential was significant. All the quadratic terms were significant.

Linear effects were jointly significant ($F(3, 16) = 15.83$, $p < 0.001$), two-way interactions ($F(3, 16) = 4.16$, $p < 0.05$ and quadratic effecs ($F(3, 16) = 35.31$, $p < 0.001$). Overall, the model was significant ($F(10, 16) = 17.87$, $p < 0.001$). Contour and perspective plots (Fig. 4) suggest we achieved the region of the optimal response near the stationary point, which was 2.64 μm length, 3.25 mM of H_2O_2 and 0.02 V. Canonical analysis confirmed that the stationary point was indeed a maximum.

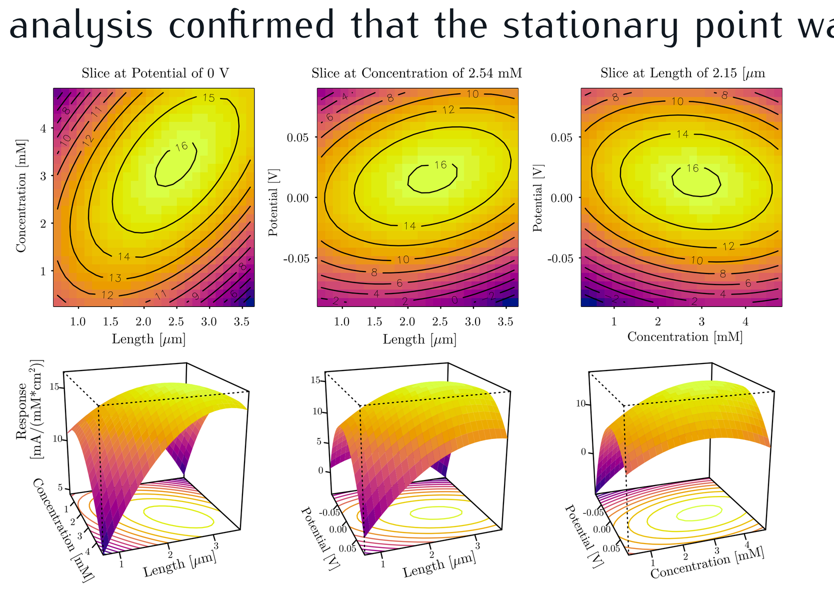

Fig.4. Contour and perspective plots of the fitted second-order model.

Characterization of the optimal design. We electrodeposited Ni between 2.6 and 3.5 min, and selected the sensor by computing the 95% CI of the nanowires in SEM images. We used a sensor with 2.6 μm (see Fig. 5), with a 95% CI of [2.48, 2.76]. The sensor response was measured width CV using H_2O_2 concentration of 0, 0.5, 1, 1.5, 2.54, 3.25 and 6.5 mM.

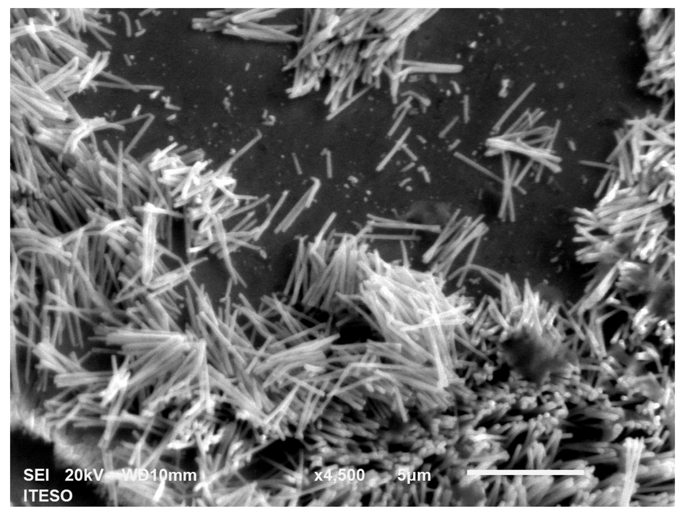

Fig. 5: SEM image of the sensor with the optimal length.

We analized the CV data as in [2, 3], interpolating the sensor response at different potentials, and then applying linear regression relating the response with concentrations, as Response$_i = \alpha_i + \beta_i \times H_2O_2$ mM.

Fig. 6**a** shows the results of this analysis. We computed the V^* at which β, the sensor sensitivity, was maximized. The response is almost linear for five concentrations (at 3.25 mM; see Fig. 6**b**).

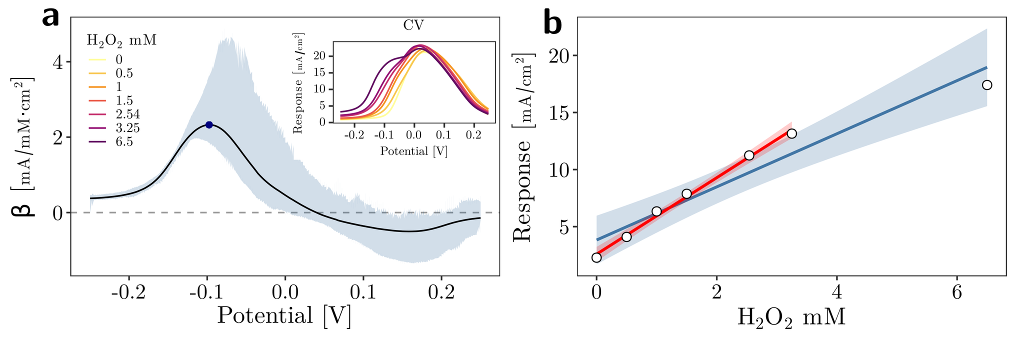

Fig. 6: Sensitivity β and linear regression at V^*. Inset in **a**: CV data.

The sensitivity, LOD and LOQ were, respectively, 3.55 mA/mMcm^2, 0.78 mM and 2.6 mM. We also measured a two more sensors for comparison: with 0μm, 0.1 mA/mMcm^2, 0.95 mM and 3.17 mM; with 0.68 μm, 1.55 mA/mMcm^2, 0.81 mM and 2.71 mM.

Conclusions

We achieved an optimal sensor design with 2.62 μm, and best-measuring conditions at 3.25 mM H_2O_2 and 0.02 V. This sensor improved the sensitivity with respect to a planar Ni sensor by a factor of 35.5, and with respect to a 0.62 μm by a factor of 3.3. The LOD and LOQ of this sensor are lower than those of the planar and 0.68 μm sensor, meaning that our optimal sensor can detect lower concentrations of H_2O_2 with higher reliability. Our results showed that RSM is a suitable and efficient approach for sensor optimization.

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