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# Electron Transfer Dynamics on Phosphazene-passivated InP Surfaces: A Study with Polyoxotungstate Complexes

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## Abstract

This study investigates the electrochemical behaviour of Indium Phosphide (InP) electrodes, both deoxidised and passivated with a phosphazene film, in the presence of redox couples in an aqueous sulfuric acid solution. The focus is on the interaction between the polyoxotungstate complex and InP electrodes, highlighting the distinct electrochemical behaviour introduced by phosphazene passivation. The results show that the passivated InP surface exhibits a higher overpotential (400mV) and a significant loss of electrochemical reversibility compared to the deoxidised surface. Despite these changes, X-ray Photoelectron Spectroscopy (XPS) analysis confirms the stability of the phosphazene film after electrochemical testing, pointing to its robustness in preventing degradation.

**Keywords:** Cyclic Voltammetry, Electrochemical Performance, InP, Semiconductor Passivation

## 1. Introduction

III-V compound semiconductors, especially InP, are increasingly valued for their exceptional intrinsic properties, such as high electron mobility and a direct bandgap, which enable applications in optoelectronics, fast digital electronics, and microwave power electronics[1]. These characteristics enable a wide range of applications in diverse fields, including fast digital and analogue microelectronics, microwave power electronics, and integrated optoelectronics[2]. However, as device miniaturisation and planar integration continue to advance, surfaces and interfaces have become critical to device performance, as they can significantly affect their functionality[3]. In practice, these interfaces are often plagued by localised states and various defects (impurities, stoichiometry defects), limiting their ability to effectively confine carriers[4]. To mitigate these negative effects, various passivation techniques have been developed to enhance the electrical properties of surfaces and interfaces, ensuring stable and optimal device performance[5].

Electrochemistry on Semiconductors (SC) plays a central role in electrochemical science due to its ability to generate processes involving majority and/or minority carriers, as well as the physical and chemical modularity of SC/electrolyte junctions[6]. These junctions behave similarly to Schottky barriers, where carrier transfer is facilitated by electrochemical processes influenced by adjustable parameters such as pH, temperature, and the presence of electroactive species in the electrolyte[7]. This allows for the control of electrochemical responses and enables chemical modification of semiconductor surfaces, which is particularly useful in optoelectronic device technologies[8]. Additionally, impedance measurements provide key

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parameters, such as junction capacitance, which is crucial for predicting the availability of free carriers at the interface[9].

In this context, Polyoxometalates (POM) stand out due to their unique redox properties, which allow them to undergo multiple oxidation and reduction cycles while maintaining a stable molecular structure[10]. POM are complex metal-oxygen anions, primarily composed of transition metals such as molybdenum, tungsten, or vanadium. Their redox behaviour makes them particularly valuable in electrochemical systems, where they act as redox mediators, facilitating electron transfer in complex systems[11]. These properties, which can be tailored by structural modifications, present promising applications for the passivation of semiconductor surfaces[12]. By inhibiting carrier recombination reactions at the interface and enhancing chemical stability, POM help improve the performance of optoelectronic devices[13].

In this work, we describe the cathodic behaviour of indium phosphide electrodes, both covered and uncovered with a phosphazene film, in the presence of redox couples in an aqueous sulfuric acid solution. This study investigates the electrochemical properties of deoxidised and phosphazene-passivated InP electrodes in an acidic solution containing polyoxotungstate complexes. The goal is to understand the impact of surface passivation on the electron transfer kinetics and overall electrochemical performance of these electrodes.

## 2. Experimental Methods

The results presented below were obtained using indium phosphide monocrystals with a surface orientation of <100>. The concentration of majority carriers (electrons) is ND = $2\times10^{18}$ atoms/cm$^3$. The mechano-chemical etching method using bromomethanol ($MeOHBr_2$) was used to prepare the deoxidised electrode. This etching method leads to reproducible behaviour of the electrodes in electrochemical studies and XPS.

The acidic buffered media (pH = 0.3) used were first prepared from ultrapure water and a concentrated sulfuric acid solution. Subsequently, different concentrations of polyoxotungstate solutions were prepared from the acid solution. The solutions were deoxygenated before recording the curves.

The reference electrode used experimentally was a mercury sulfate electrode, and the counter-electrode was a platinum wire. Passivated electrodes were obtained by chronopotentiometry in liquid ammonia[14].

All experiments were performed in the dark, using 2273 parstat. *In-situ* capacitance measurements were performed at a frequency of 1.03kHz.

## 3. Results and Discussion

The study investigates the electrochemical behaviour of deoxidised and passivated InP electrodes using cyclic voltammetry with a solid-state complex that has a Keggin-type structure in buffered acidic conditions.

When immersed in solution, the electrode reaches an equilibrium potential influenced by the pH, the nature of the electroactive species, and the electrode material. Polarisation begins from this open circuit potential. The methodology focused on a potential range where only the first cathodic transfer wave is observed, avoiding interference from other reduction waves.

### 3.1 Electron Transfer Kinetics of Polyoxotungstate Complex on InP Electrode Deoxidised

The current-potential curves (Figure 1) presented here were obtained using cyclic voltammetry, which measures the current resulting from redox processes at a solid electrode (InP electrodes) when a linearly varying potential is applied over time (scan rate in V/s). The potential difference relative to a reference electrode (MSE) is provided by a voltage generator, and the current is collected at the counter electrode (platinum wire), with the measurement being automatically recorded at each potential step by an electronic device (potentiostat). This time-resolved current measurement directly quantifies the rate of the kinetically determining reaction of the process[15].

Figure 1 corresponds to the voltammogram obtained from the n-type InP electrode, previously deoxidised in an $H_2SO_4$ solution containing or not containing the polyoxotungstate complex at a concentration of $10^{-4}$ mol/L. The data were recorded by varying the polarisation towards negative overpotentials at 20mV/s. The voltammogram from the raw data in the presence of the complex shows a reproducible, mono-electronic, and reversible wave in the region without current. A cathodic peak is observed at -0.49V *vs.* MSE and an anodic peak at -0.43V *vs.* MSE, characteristic of a reversible wave. The difference between the cathodic and Anodic Peak potentials (ΔEp) is equal to 59/n mV, which represents the theoretical value for a reversible (Nernstian)

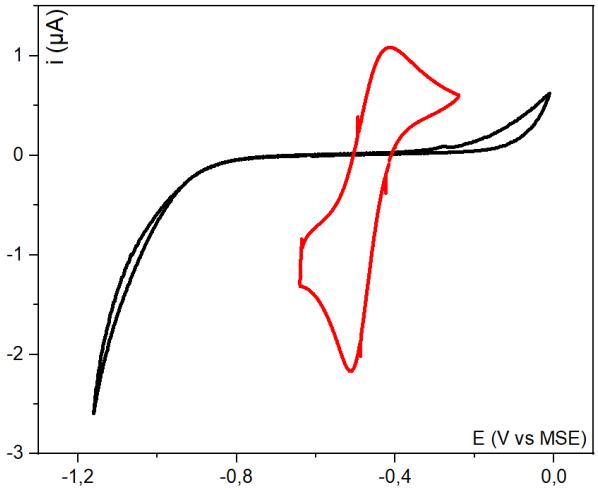



**Figure 1.** i *vs* f(E) curve in $H_2SO_4$ (black) and in the presence of the polyoxotungstate complex (red) at pH = 0.3 on n-type doped InP 10[18].

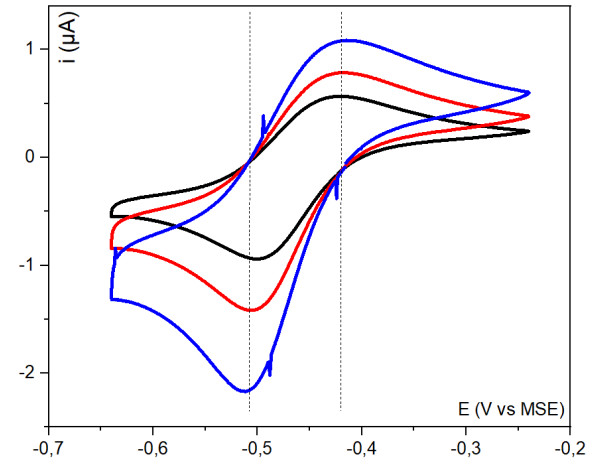



**Figure 2.** I *vs* f(E) curve in $H_2SO_4$ in the presence of the polyoxotungstate complex at v = 20 mV/s (black), v = 50 mV/s (red), v = 100 mV/s (blue) at pH = 0.3 on n-type doped InP 10[18].

process, where *n* is the number of electrons transferred. Furthermore, the mono-electronic nature of the wave is confirmed using the 59/n mV relation, with *n* = 1. The standard potential of the polyoxotungstate couple is also determined by the midpoint of the anodic and cathodic peak potentials, which is -0.46V vs. MSE. This behaviour is consistent with the literature[16].

The voltammograms in Figure 2 were recorded at different scan rates. It is important to recall that there is kinetic competition between the slowest electrochemical reaction and diffusion. The potentiostat's ability to increase the scan rate (from a fraction of V/s to several thousand V/s routinely) effectively increases the diffusion rate of molecules toward the electrode surface. This can sometimes lead to a transition from diffusion-controlled kinetics to control by a chemical or electrochemical reaction[17]. Under these conditions, it can be observed that the anodic and cathodic peak potentials are independent of the scan rate (Figure 3). Additionally, the peak current is proportional to the square root of the scan rate (Figure 4). Based on these observations, it can be stated that the

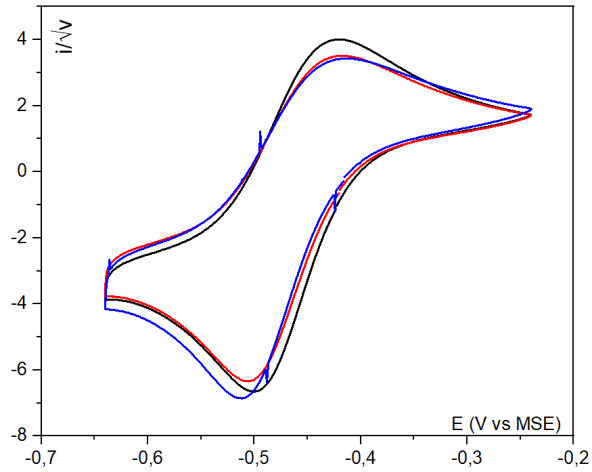



**Figure 3.** i/√v *vs* f(E) curve in $H_2SO_4$ in the presence of the polyoxotungstate complex at v = 20 mV/s (black), v = 50 mV/s (red), v = 100 mV/s (blue) at pH = 0.3 on n-type doped InP 10[18].

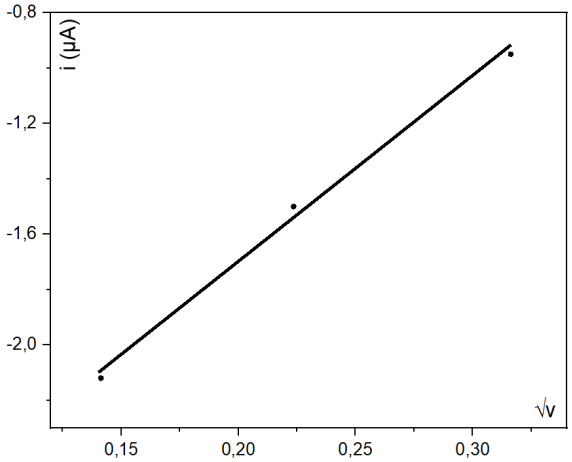



**Figure 4.** Peak intensity curve as a function of the logarithm of the scan rate i *vs* f(√v) in $H_2SO_4$ in the presence of the polyoxotungstate complex at pH = 0.3 on n-type doped InP 10[18].

electrochemical behaviour of the polyoxotungstate complex on the deoxidised InP electrode is characteristic of a system that is fast and purely diffusion-limited.

For such a system, the shape of the voltammograms suggests a fast electron transfer mechanism, which can be described by the following equations[18]:

$$I_{p,c} = 0,446FSC^0\sqrt{D}\sqrt{\frac{F\upsilon}{RT}} \quad (1)$$

$$E = E^0 - 1,11\frac{RT}{F} \quad (2)$$

Where:

$I_{p,c}$ : Peak current of the electron transfer process (A)
$F$ : Faraday constant (F = 96 485 C·mol$^{-1}$)
$S$ : Electrode surface area (cm$^2$)
$C^0$ : Initial concentration of the polyoxotungstate complex (mol·L$^{-1}$)
$D$ : Diffusion coefficient of the polyoxotungstate complex (cm$^2$.s$^{-1}$)
$\upsilon$ : scan rate (V·s$^{-1}$)
$R$: Ideal gas constant (R= 8,314 J·mol$^{-1}$·K$^{-1}$)
$T$: Temperature (K)
$E$: applied potential (V)
$E^0$ : Redox potential of the polyoxotungstate complex (V)

The diffusion coefficient $D$ of the polyoxotungstate complex is directly determined using the slope of the curve shown in Figure 4. Figure 4 depicts the cathodic peak current $I_{p,c}$ as a function of the square root of the scan rate.

The slope p of the curve $I_{p,c} = f(\sqrt{v})$ is given by:

$$p = 6,633\times10^{-6} = 0,446FSC^0\sqrt{D}\sqrt{\frac{F}{RT}} \quad (2)$$

Given the values of concentration $C^0 = 10^{-4}$ *mol/L* and the working electrode surface area $S = 2.10^{-2}$ *cm*$^2$, the diffusion coefficient D is calculated to be $D = 1,26 \times 10^{-5}$ *cm*$^2$.*s*$^{-1}$.

## 3.2 Electron Transfer Kinetics of Polyoxotungstate Complex on InP Electrode Modified with Polyphosphazene Film

The electron transfer kinetics between the polyoxotungstate complex and the InP electrode were studied when the electrode was coated with a polyphosphazene film. As shown in the results of Figure 5, the experiment with the modified electrode displays a single wave in cyclic voltammetry. This single wave is not the result of a dissociative electron transfer, meaning a charge transfer reaction coupled with a chemical reaction or bond cleavage.

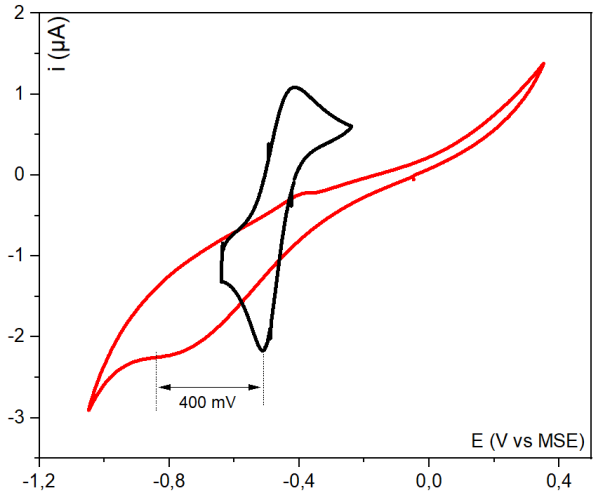



**Figure 5.** i *vs* f(E) curve in $H_2SO_4$ in the presence of the polyoxotungstate complex at pH = 0.3 on n-type doped InP $10^{18}$ deoxidised (black) and passivated (red).

Thus, the oxidation of the reduced form of the complex becomes difficult, or even impossible, on the InP electrode due to the presence of the polyphosphazene film. This result can be explained by the strong presence of delocalised electrons in the polyphosphazene film, which causes a screening effect that hinders electron addition from the electrolyte to the conduction band of the semiconductor.

It is also noted that the cathodic peak potential obtained with the modified electrode is more negative (in absolute value) compared to the deoxidised electrode. This negative overpotential observed with the phosphazene film contradicts the results of the energy study, which clearly states that the presence of the film on InP should modify the band curvature by bringing the conduction band closer to flat band or accumulation conditions, requiring less energy for the electrochemical reduction of the complex[19].

In reality, beyond considering the energy parameter, it is essential to account for the conductivity of the passivating film under these conditions (flat band or accumulation on passivated InP)[20]. Additionally, we know that the scan rate significantly influences the shape of current-potential curves. When the scan rate increases, the peak potentials of the reduction wave deviate, and the normalised peak current decreases (Figure 6), in contrast to what was

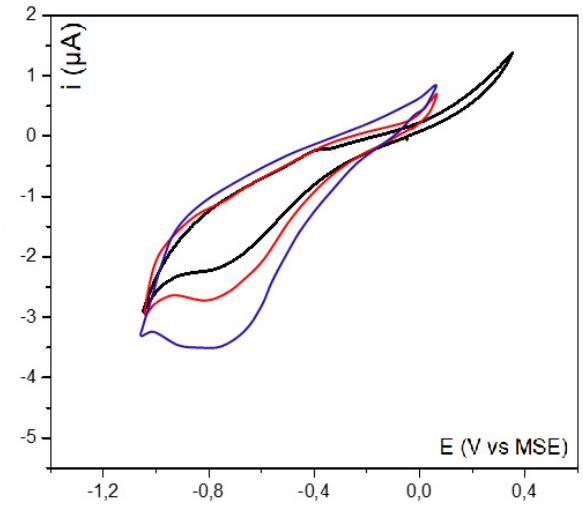



**Figure 6.** i *vs* f(E) curve in $H_2SO_4$ in the presence of the polyoxotungstate complex at v = 20 mV/s (black), v = 50 mV/s (red), v = 100 mV/s (blue) at pH = 0.3 on passivated n-type doped InP $10^{18}$.

observed for the deoxidised electrode. These observations indicate that the reaction is kinetically controlled by the initial electron transfer step, and Nernst's law is no longer applicable for the concentrations at the electrode.

The transfer coefficient α can then be calculated from the wave width at half-height or from the slope of the peak potential variation as a function of the scan rate, since the behaviour of the passivated InP electrode in the presence of the polyoxotungstate complex is characteristic of a slow transfer.

The electron transfer of the polyoxotungstate complex is slow on the passivated electrode, while it is fast on the deoxidised electrode. Therefore, the Hush-Marcus model is suitable for describing the charge transfer reactions between the polyoxotungstate complex and the passivated InP electrode, as it allows for the description of outer-sphere charge transfers, *i.e.*, without significant changes in the molecular structure. The rate constant $k_{et}$ for electron transfer from a semiconductor to an outer-sphere redox species in solution can be expressed as follows[21,22]:

$$D = 1{,}26 \times 10^{-5}\, cm^2.s^{-1} \qquad (4)$$

Where:

$\upsilon_n$ : Vibrational frequency associated with electron transfer

$\kappa_{el}$ : Electronic coupling between the donor and acceptor

$\kappa_n$ : is the nuclear term describing the Franck-Condon factors of the charge transfer reaction and is defined by relation 5[22, 23]:

$$\kappa_n = \exp\left(\frac{(\Delta G^{\circ} + \lambda)^2}{4\lambda kT}\right) \qquad (5)$$

Various methods are currently used to estimate the electron transfer constant $\kappa_{et}$ at the semiconductor/electrolyte interface. We use the method proposed by N. Lewis *et al.*[21]. In their work, the authors describe a method for estimating $\kappa_{et}$ from an n-type InP electrode in contact with molecular redox acceptor species in outer-sphere form, dissolved in various concentrations in a given solution. They use the electron density as a function of $\kappa_{et}$

$$J_{et} = qk_{et}\, n_s\, (E)[A] \qquad (6)$$

In this equation, $J_{et}$ is the current density associated with the electron transfer process, $q(C)$ is the elementary charge, $n_s(cm^{-3})$ is the electron concentration at the semiconductor surface, and $[A](cm^{-3})$ is the concentration of acceptors involved in the electron transfer process.

Using Mott-Schottky plots, the number of dopants was determined. The calculated value is in good agreement with the supplier's dopant count. In addition to the number of dopants, the Mott-Schottky plot allows access to the flat band potential. These data, combined with the current-potential curves, allow the evaluation of the charge transfer constant $\kappa_{et}$ for the InP/polyoxotungstate system:

$$k_{et} = 0{,}0625\ cm^4.s^{-1}$$

The combination of energetic and kinetic measurements was used to estimate the charge transfer rate constant for the passivated InP junction in contact with a polyoxotungstate complex dissolved in $H_2SO_4$.

## 3.3 Post-electrochemical Study and XPS Analysis

Following the electrochemical study, the electrode was carefully removed from the cell, rinsed with ultrapure water, and dried under a gentle flow of argon. The sample, placed in a tube filled with argon, was then transferred to the XPS analysis chamber. This procedure of transporting the sample under an inert atmosphere was used for all XPS analyses in this work to minimise the risk of sample contamination. Similar to the previous chemical analysis of the sample surface, we focused solely on the spectral responses of indium, phosphorus, and nitrogen elements.

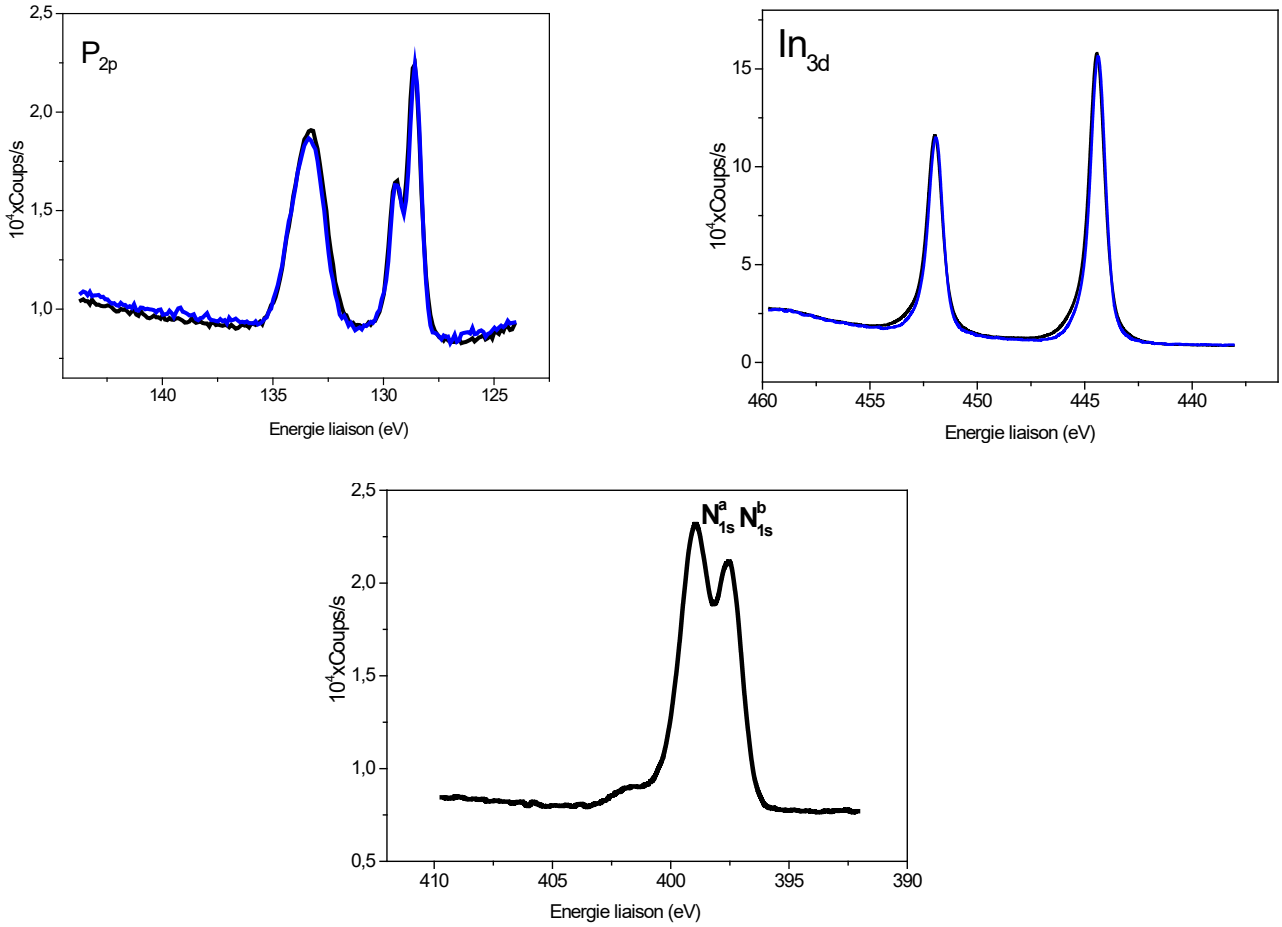



**Figure 7.** XPS spectrum of the passivated InP surface before and after the kinetic study.

Figure 7 shows the XPS spectra of the 3d, 2p, and 1s orbitals of the InP surface recorded before and after the kinetic study. It can be observed that the peak energies of the two components, $3d_{5/2}$ and $3d_{3/2}$, of indium remain unchanged. Additionally, there are no significant changes in the spectra of the phosphorus and nitrogen components. This surprising and encouraging result reflects the stability of the phosphazene film on the electrode surface.

Moreover, it is important to note that traces of tungsten appear in the general spectrum. At this stage, we cannot precisely determine the exact nature of the interactions between the phosphazene film and the tungstate complex. Further studies will need to be conducted to verify the nature of the bonds (chemisorption or physisorption).

## 4. Conclusion

Electrochemical studies revealed distinct differences in the behaviour of deoxidised and phosphazene-passivated InP electrodes in the presence of polyoxotungstate complexes. Passivation with a phosphazene film resulted in an increased overpotential and a loss of electrochemical reversibility. However, XPS analysis confirmed the robustness of the phosphazene film, which remained intact after electrochemical testing. These findings suggest that phosphazene films offer stable surface protection but may hinder electron transfer processes due to a screening effect. Further studies are required to explore the nature of interactions between the polyoxotungstate complex and the phosphazene film, particularly in distinguishing between chemisorption and physisorption.

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