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## Determination of Silver-Modified Titanium Phosphate Nanoparticles by Voltammetric and Electrocatalytic Methods

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First published: 14 November 2014 | <https://doi.org/10.1002/elan.201400519> | Cited by:4

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# Determination of silver-modified titanium phosphate nanoparticles by voltammetric and electrocatalytic methods

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Received: ((will be filled in by the editorial staff))

Accepted: ((will be filled in by the editorial staff))

## Abstract

The electrochemical determination of silver-modified titanium phosphate nanoparticles (Ag-TiPNPs) was performed using two electrochemical features of this novel kind of nanoparticles. First, a determination using the voltammetric activity of the silver from the Ag-TiPNPs was carried out. Secondly, the electrocatalytic effect of Ag-TiPNPs was shown for the first time to the hydrogen evolution reaction (HER) and the determination of these nanoparticles was performed by chronoamperometry using this electrocatalysis. Moreover, it was verified that the catalytic effect was due to the electroreduced silver since the unmodified titanium phosphate nanoparticles (TiPNPs) did not exhibit this effect. Detection limits as low as 0.1 and 0.75 ng  $\mu\text{L}^{-1}$  of Ag-TiPNPs were obtained with the voltammetric and chronoamperometric methods, respectively. 8-channel screen-printed electrochemical arrays (8xSPCEs) were employed as transducers to carry out these electrochemical studies, due to its low cost and time saving.

**Keywords:** Nanoparticles; Metal-based nanoparticles; Electrocatalysis; Catalysis; Hydrogen evolution reaction

DOI: 10.1002/elan.((will be filled in by the editorial staff))

## 1. Introduction

Nanotechnology is a wide field progressing at a fast pace. The development of new nanomaterials introducing exciting features or improving the characteristics of the materials known to date. Therefore, its characterization and the search of new applications for these new nanomaterials is of utmost importance in different scientific disciplines such as electrochemistry. Special attention has been placed on the use of nanomaterials for several applications such as electrochemical batteries[1], energy storage[2], and also for electroanalytical applications, specially in the development of (bio)sensors resulting on improved transducers[3] or novel electrochemical labels[4–6].

Several metal-based nanoparticles such as gold nanoparticles (AuNPs)[7,8], platinum nanoparticles (PtNPs)[9], silver nanoparticles (AgNPs)[10] or quantum dots[11], among many others, have been characterized by electrochemical techniques. Titanium phosphate nanoparticles are novel nanoparticles with two main applications: heavy-metal removal from waters[12], and

electrochemical labelling for biosensors[13–15]. These two very different kinds of applications make use of the ability of the TiPNPs to work as a cation exchanger, which easily allow its modification with different metals. However, an electrochemical method for the quantification of these nanoparticles, which could be useful for the synthesis control, has not been published.

In the other hand, several metal nanoparticles generally show a catalytic effect to some electrochemical reactions such as the reduction of  $\text{H}_2\text{O}_2$  by PtNPs[16] or the oxidation of sugars by NiNPs[17]. AuNPs also show an electrocatalytic effect towards HER allowing its use for the quantification of AuNPs[18] or its application in biosensors[19–21]. However, no electrocatalytic effect of the TiPNPs has been published to date.

In this paper, we make use of low-cost 8-channel screen-printed electrochemical arrays to quantify Ag-TiPNPs by a voltammetric method. We study the electrocatalytic effect of these nanoparticles on the HER in acidic media and apply this effect to the determination of Ag-TiPNPs by chronoamperometry.

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## 2. Experimental

## 2.1. Apparatus and electrodes

Voltammetric measurements were performed with a  $\mu$ Stat 8000 (DropSens, Spain) potentiostat interfaced to a Pentium 4 2.4 GHz computer system and controlled by DropView 8400 1.0 software. All measurements were carried out at room temperature. 8-channel screen-printed electrochemical arrays were purchased from DropSens (Spain). Each array is formed by eight 3-electrode electrochemical cells (25  $\mu$ L volume) with carbon-based working and counter electrodes, whereas pseudoreference electrodes and electric contacts are made of silver. This device has dimensions of 4.0 x 7.9 x 0.06 cm (length x width x height) and the diameter of the working electrodes is 2.56 mm. The 8-channel arrays were connected to the potentiostat through a specific connector, DRP-CAST1X8 (Fig. 1). An Elmasonic P ultrasonic bath (Elma GmbH, Germany) was also employed to disperse the nanoparticles in the solution. A JEOL 6610LV scanning electron microscope (30 kV, Japan) was used to characterize the working electrodes.



Fig. 1. Image of an 8-channel electrochemical screen-printed array.

## 2.2. Reagents and solutions

Sulfuric acid (97%), acetic acid (100%), nitric acid (65%), fuming hydrochloric acid (37%), perchloric acid (70%), ammonia solution (25%), dried ethanol, silver nitrate, potassium iodide and potassium chloride were purchased from Merck (Spain). Phosphoric acid ( $\text{H}_3\text{PO}_4$ , crystalline), docusate sodium salt (AOT) and titanium(IV) butoxide (TBOT) were purchased from Sigma-Aldrich (Spain). Ultrapure water obtained with a Millipore Direct Q5™ purification system from Millipore Ibérica S.A. (Madrid, Spain) was used throughout this work. All other reagents were of analytical grade. Working solutions of TiPNPs and Ag-TiPNPs were made

in ultrapure water, and sonication was used to obtain homogenous nanoparticle colloidal suspensions.

## 2.3. Synthesis of titanium phosphate nanoparticles

Synthesis of titanium phosphate nanoparticles was carried out following a procedure found in the literature[22]. Typically, 5.65 mmol of AOT was dissolved into 12.5 g of ethanol and  $\text{H}_3\text{PO}_4$  (51 mmol) was added. This solution was filtered and the precipitate was removed. Then, a mixture of TBOT in ethanol (2.5mmol/15.5 mL) was fast dropped into the filtered solution, and stirred at 80 °C for 6 h. A white solid product is obtained and washed with ethanol and ultrapure water for several times until neutral pH. Silver-modified titanium phosphate nanoparticles were synthesized by means of an ionic exchange mechanism following a procedure found in the literature[13]. Briefly, 1 mL of TiPNPs (40 mg  $\text{mL}^{-1}$ ) was dispersed in 17 mL of 10 mM  $\text{AgNO}_3$  aqueous solution and stirred at 50 °C for 24 h. In these conditions the maximum load of silver is achieved. Ag-TiPNPs were obtained after centrifugation and washing several times with ultrapure water.

## 2.4. Modification of 8xSPCEs with TiPNPs

Modification of 8xSPCEs with TiPNPs was carried out by depositing an aliquot of 2  $\mu$ L of the TiPNPs solution on the working electrode surface. The solution was left at room temperature (20°C) until dryness.

## 2.5. Electrochemical measurements

For the voltammetric determination, a constant potential of -0.2 V was applied for 180 s for the preconcentration of silver on the electrode surface. Then, the potential was swept from -0.2V to +0.4 V using square-wave voltammetry with the optimized parameters (5 mV step potential, 30 Hz frequency, 10 mV amplitude). The analytical signal corresponded to the peak current obtained after the stripping of the preconcentrated silver. Chronoamperometry was carried out by applying a specific potential during a period of time. The value of the cathodic current at 150 s is considered as the analytical signal for the chronoamperometric measurements. All measurements were performed without removing oxygen from the solution, and at run temperature (24 $\pm$ 2 °C).

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## 3. Results and discussion

## 3.1. Voltammetric quantification of Ag-TiPNPs

Metal-modified TiPNPs can be measured with electrochemical techniques if the metal has an electroactive character. Cyclic voltammetry (CV) measurements were carried out for 8xSPCEs unmodified and modified with different concentrations of Ag-TiPNPs ( $0.2$ ,  $2$  and  $20 \mu\text{g } \mu\text{L}^{-1}$ ) from  $+0.6$  V to  $-0.8$  V ( $50 \text{ mV/s}$ ). Typical anodic (at  $+0.05$  V) signals for the oxidation of silver were obtained as shown in Fig. 2A. Peak current increased with the amount of Ag-TiPNPs. Although no clear cathodic signals for the reduction of silver were obtained, small reduction processes can be seen with higher amounts of Ag-TiPNPs at a potential about  $-0.25$  V right before the broad background signal. Therefore, the silver introduced in the structure of the TiPNPs can be detected being the oxidation peak the most useful for the determination of Ag-TiPNPs.

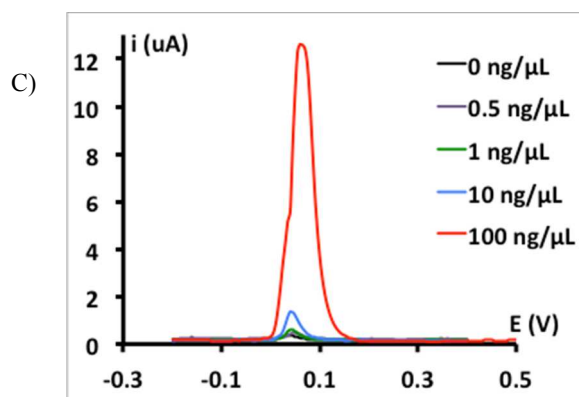
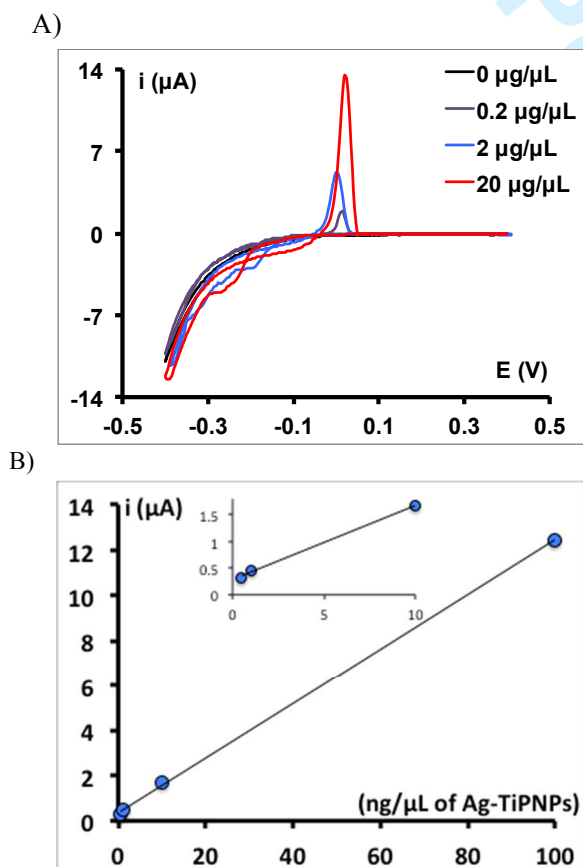
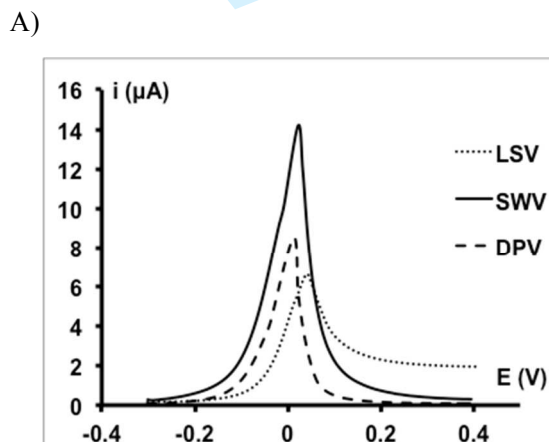


Fig. 2. **A)** CVs for different amounts ( $0$ ,  $0.2$ ,  $2$  and  $20 \mu\text{g } \mu\text{L}^{-1}$ ) of Ag-TiPNPs in  $0.1 \text{ M KI}$ . **B)** Square-wave voltammograms (SWVs) for  $0$ ,  $0.5$ ,  $1$ ,  $10$  and  $100 \text{ ng } \mu\text{L}^{-1}$  of Ag-TiPNPs with the optimized conditions. **C)** Calibration plot representing the analytical signal vs. the amount of Ag-TiPNPs for the square-wave voltammograms. Inset: same plot but magnifying the range for low amounts of Ag-TiPNPs.

A stripping voltammetric method was optimized for the determination of Ag-TiPNPs. 8xSPCEs were modified with  $2 \mu\text{L}$  of Ag-TiPNPs with a concentration of  $10 \text{ ng } \mu\text{L}^{-1}$  ( $20 \text{ ng}$  of Ag-TiPNPs). The different parameters that could have an effect on the analytical signal as the electrochemical technique of the stripping step (Fig. 3A), electrolytic medium (Fig. 3B), the potential and time of deposition and other parameters of the electrochemical technique were optimized. Square-wave voltammetry using a deposition potential of  $-0.2$  V during  $180 \text{ s}$  in a  $0.1 \text{ M KI}$  solution were chosen as the most useful experimental conditions. All optimized values are shown in Table 1.





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B)

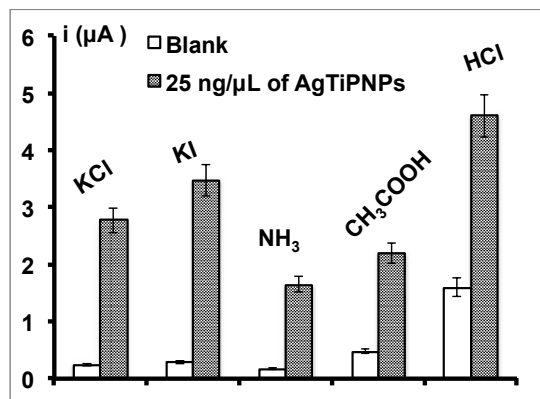


Fig. 3. A) Linear sweep, differential-pulse and square-wave voltammograms for  $0.5 \mu\text{g } \mu\text{L}^{-1}$  of AgTiPNPs after silver deposition for 30 s at  $-0.3 \text{ V}$ . Electrolytic medium:  $0.1 \text{ M KI}$ . B) Signal/background peak currents of  $25 \text{ ng } \mu\text{L}^{-1}$  of AgTiPNPs in several  $0.1 \text{ M}$  electrolytic media. Experimental conditions: square-wave voltammetry with a deposition potential of  $-0.3 \text{ V}$  for 30 s.

Table 1. Optimized parameters for the square-wave anodic stripping voltammetry.

$t_{\text{dep}}$	$E_{\text{dep}}$	Eq. time	Step	Frequency	Amplitude
180 s	$-0.2 \text{ V}$	5 s	5 mV	30 Hz	10 mV

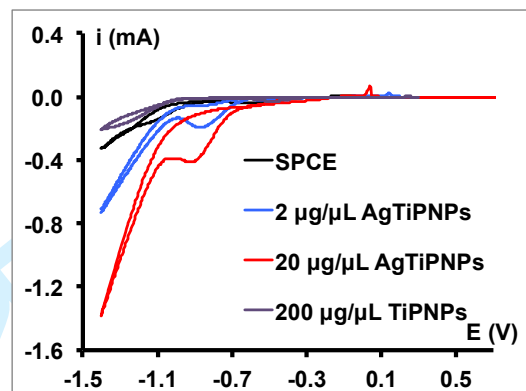
After the optimization of parameters, a calibration curve for different amounts of Ag-TiPNPs deposited on the electrodes was performed (Fig. 2B). The analytical signal is directly proportional to the amount of Ag-TiPNPs (Fig. 2C), resulting in a linear relationship in the range between 1 and 200 ng of Ag-TiPNPs following the equation:  $i(\mu\text{A}) = 0.28 + 0.12 \cdot (\text{ng } \mu\text{L}^{-1} \text{ of Ag-TiPNPs})$ ,  $R^2 = 0.998$ ,  $n=3$ . A detection limit of  $0.1 \text{ ng } \mu\text{L}^{-1}$  of Ag-TiPNPs (calculated as three times the standard deviation of the estimate) and a RSD of 5.4% ( $n=3$ ) were obtained.

### 3.2. Electrocatalytic effect and chronoamperometric quantification of AgTiPNPs

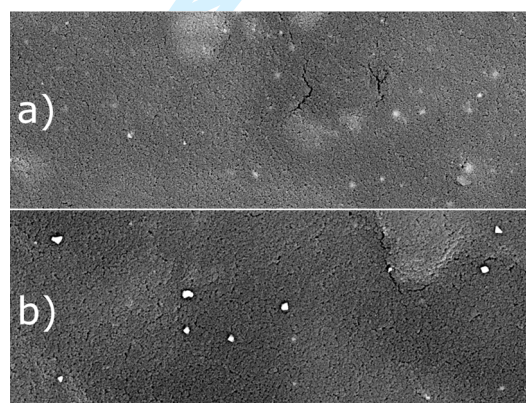
CV measurements were performed for unmodified 8xSPCEs and modified with TiPNPs and Ag-TiPNPs (Fig. 4A) from  $+0.4 \text{ V}$  to  $-1.4 \text{ V}$  in a solution of  $1 \text{ M HCl}$ . A clear difference between the reduction curves from unmodified electrodes and modified with different amounts of Ag-TiPNPs is shown. The cathodic current of the reduction of protons increased with the amount of Ag-TiPNPs that shows an increment in the reaction rate of the HER. The electrocatalytic effect of Ag-TiPNPs to

the HER in an acidic solution is observed. Fig. 4A also showed that no electrocatalytic effect is generated using unmodified TiPNPs. Therefore, we concluded that the electrocatalytic effect could be produced by the Ag that is bound to the structure of the TiPNPs. By applying the reduction potential to produce the HER, Ag(I) is reduced and elemental Ag is being formed (with nanoparticle shape) on the electrode surface (Scheme 1). SEM images of the Ag-TiPNPs modified electrode and Ag-TiPNPs modified electrode after reduction are shown in Figure 4Ba and 4Bb, respectively. For the Ag-TiPNPs modified electrode, silver can be seen with a brighter color but inside the TiPNPs structure, but after the reduction, silver nanoparticles are perfectly visible above the TiPNPs surface. However, silver nanoparticles could also be below the TiPNPs surface on the carbon electrode. Probably, the electrocatalytic effect to the HER shown by Ag-TiPNPs is due to the silver nanoparticles formed. This results are consistent with other studies that have shown this catalytic effect of silver to the HER[23].

A)



B)



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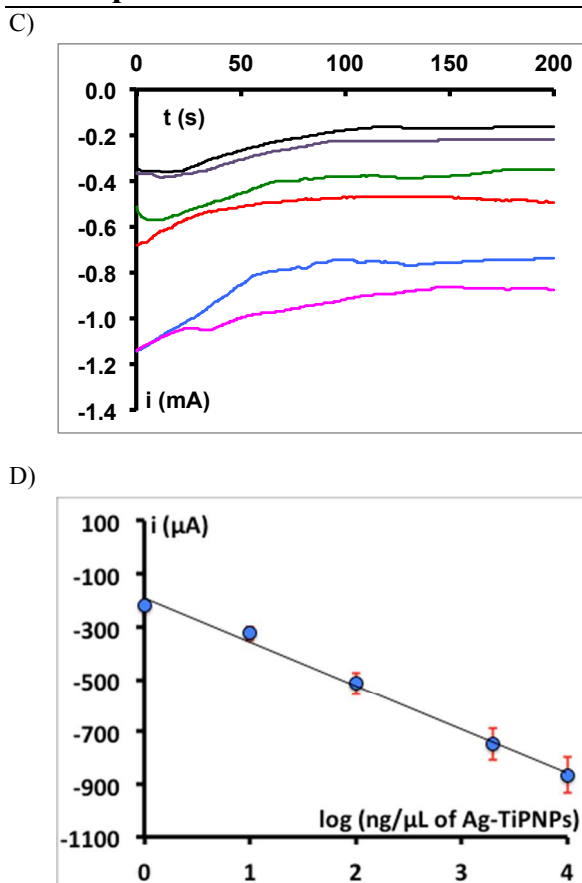
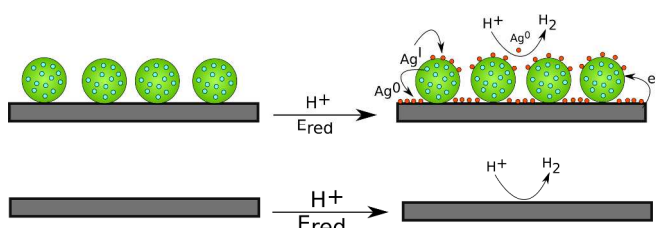


Fig. 4. **A)** CVs for different amounts (0, 2 and 20  $\mu\text{g } \mu\text{L}^{-1}$ ) of Ag-TiPNPs and 200  $\mu\text{g } \mu\text{L}^{-1}$  of TiPNPs in 1 M HCl. **B)** SEM images of working electrodes a) modified with Ag-TiPNPs and b) modified with Ag-TiPNPs after reduction. **C)** Chronoamperometric curves for 0.001, 0.01, 0.1, 2 and 10  $\mu\text{g } \mu\text{L}^{-1}$  of Ag-TiPNPs in 1 M HCl after applying a fixed potential of -1.2 V. **D)** Calibration plot representing the analytical signal vs. the logarithm of the amount (in  $\text{ng } \mu\text{L}^{-1}$ ) of Ag-TiPNPs for the chronoamperometric measurements at 150 s.



Scheme 1. Schematic diagram of electrochemical HER catalyzed by Ag-TiPNPs (top) and not catalyzed (bottom).

The electrocatalytic effect can also be measured by chronoamperometry applying an adequate reduction potential where the protons in the acidic medium are catalytically reduced to hydrogen in presence of Ag-TiPNPs. Several parameters that could affect the analytical signal obtained by chronoamperometry such as the reduction potential (Fig. 5A) and the type and

concentration of acid (Fig. 5B) were optimized. The best results in terms of signal/background were obtained with 1M HCl and, therefore, it was chosen as the most suitable acidic medium. The optimum reduction potential in terms of signal/background ratio was -1.2 V. The analytical signal considered was the generated cathodic current at a time of 150 s (Fig. 4C), because at this time the current was already stabilized. After this optimization, a series of experiments were carried out to obtain a calibration curve. The analytical signal is related to the logarithm of the amount of Ag-TiPNPs (Fig. 4D), resulting in a linear relationship in the range between 1  $\text{ng } \mu\text{L}^{-1}$  and 10  $\mu\text{g } \mu\text{L}^{-1}$  of Ag-TiPNPs according to the following equation:  $i (\mu\text{A}) = -191.3 + 166.7 \cdot \log (\text{ng } \mu\text{L}^{-1} \text{ of Ag-TiPNPs})$ ,  $R^2=0.993$ ,  $n=3$ . A detection limit of 0.75  $\text{ng } \mu\text{L}^{-1}$  of Ag-TiPNPs and a RSD of 8.9% ( $n=3$ ) were obtained. The detection limit was calculated as the amount that gives an analytical signal obtained after adding to the blank signal three times the standard deviation of this signal.

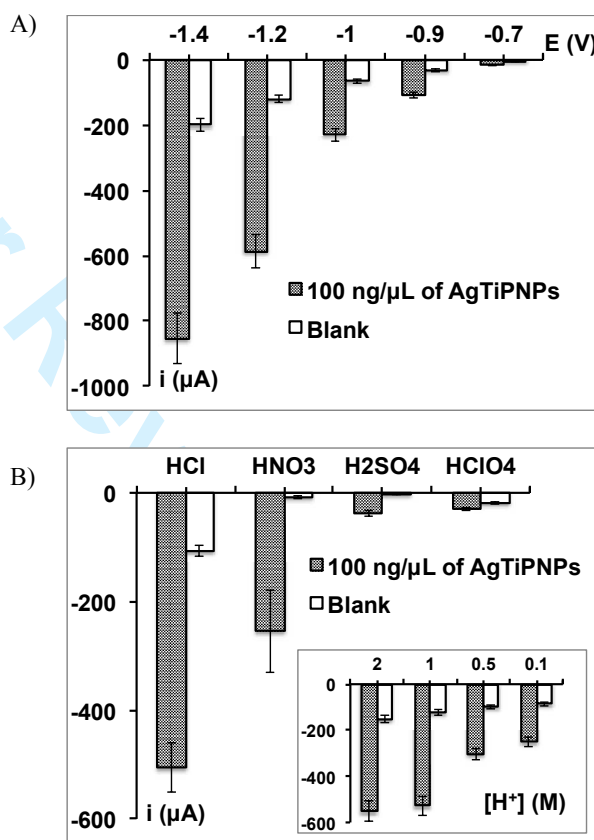


Fig. 5. **A)** Signal/background currents for CA experiments for different reduction potentials with 100  $\text{ng } \mu\text{L}^{-1}$  of AgTiPNPs in 0.1 M HCl. **B)** Signal/background currents for CA measurements for different types of acid (0.1 M) with 100  $\text{ng } \mu\text{L}^{-1}$  of AgTiPNPs ( $E_{\text{red}}: -1.2\text{V}$ ). Inset: signal/background currents for CA measurements for several concentrations of HCl ( $E_{\text{red}}: -1.2\text{V}$ ).

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Similar analytical characteristics were obtained with both methods. Although a lower LOD was obtained with the voltammetric method, the lower value of the linear range is comparable (0.5 versus 1 ng  $\mu\text{L}^{-1}$  of AgTiPNPs). However, the voltammetric method has the advantage of using a longer deposition time to improve the LOD and the sensitivity. Regarding the analysis time, similar times are necessary to make the determination of AgTiPNPs by both methods. Moreover, the low pH medium for the electrocatalytic method (1 M HCl) may be useful for certain applications.

## 4. Conclusions

In this paper, we have shown some interesting electrochemical features presented by Ag-TiPNPs. First, we have developed a voltammetric method for the fast and sensitive determination of Ag-TiPNPs making use of the voltammetric activity of the Ag(I) inside the TiPNPs structure. On the other hand, the electrocatalytic effect of metal-modified TiPNPs to the HER was shown for the first time. A method was developed to quantify Ag-TiPNPs by chronoamperometry with similar figures of merit to the voltammetric method due to the catalytic effect.

Both methods presented in this work may have basic applications such as quantifying the amount of TiPNPs in a sample, perform a control of the synthesis of TiPNPs, and in biosensing applications used as electrochemical labels. We have developed two electrochemical methods that can work for this kind of applications. We think that similar results to those presented in this work could be obtained with TiPNPs modified with other metals.

The use of metal-modified TiPNPs opens the door to a new set of methodologies for electroanalytical applications. Its easy synthesis together with its low price and the ability to be modified with almost any metal, make the TiPNPs very interesting for the development of electrochemical biosensors.

## 5. Acknowledgements

This work has been supported by the MICINN-12-CTQ2011-24560 project from the Spanish Ministry of Economy and Competitiveness (MEC). Daniel Martín-Yerga thanks the MEC for the award of a FPI grant (BES-2011-054408).

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