

## Facile Method for the Construction of Random Nanoparticle Arrays on a Carbon Support for the Development of Well-defined Catalytic Surfaces

Ronan Baron, Fallyn W. Campbell, Ian Streeter, Lei Xiao and, Richard G. Compton\*

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ (UK).

\*E-mail: [richard.compton@chem.ox.ac.uk](mailto:richard.compton@chem.ox.ac.uk)

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A simple and easy way to construct platinum nanoparticle (PtNPs) arrays on a carbon matrix is presented and the catalytic properties of the developed materials are evidenced with electrochemical studies. Technically, the key point resides in being able to get metallic nanoparticles of homogeneous size that are well dispersed on a carbon substrate. Specific efforts in this direction led us, here, to obtain, for the first time, well-defined and well-spread PtNPs of  $100 \pm 40$  nm on carbon microspheres. The resulting material was used for the development of a low cost practical Pt nanoelectrode array sensor for aqueous proton detection. In addition, methanol oxidation was studied to exemplify potential uses in fuel cells. The procedures described are very simple to apply and represent an original strategy for the development of well-defined catalytic surfaces.

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**Keywords:** Nanoparticle Arrays; Nanoelectrodes ; Nanoelectrode Ensembles; Proton reduction, pH determination

### 1. INTRODUCTION

The recent breakthroughs made in the field of nanotechnologies led, in the last few years, to the development of diverse nanosized objects. More especially, considerable efforts have been devoted to the development of catalytic surfaces made of nanoparticle arrays [1]. In the field of electrochemistry, nanoparticle arrays were developed as catalytic surfaces for fuel cells and the concept of nanoelectrode arrays was introduced [2]. The reduction in size of an electrode up to the nanoscale considerably improves the mass transport because of the contribution of the radial diffusion and the signal to noise ratio because of the lower internal resistance ( $iR$ ). Hence, nanoelectrodes are particularly well suited for fast scan voltammetry experiments, electroanalytical applications and electrochemical

measurements in viscous media. The construction of nanoelectrodes generally involves procedures like chemical vapor deposition and photolithography [3], electron-beam lithography [4] or electroless deposition in polycarbonate membranes [5]. These methods allow, in general, the precise control of the nanoelectrode or nanoelectrode arrays geometry. However, they require specialized equipment that are relatively complex to implement (except for polycarbonate membranes [5]) and they are not adapted for the production of a large number of pieces. The production of low price nanoelectrodes and nanoelectrode arrays then remains a challenging issue. Another approach to the construction of nanoparticle arrays as catalytic surfaces is presented in this manuscript. Metallic nanoparticles are synthesized on a conductive carbon support to get a random nanoparticle array. The association of metallic nanoparticles to bulk carbon substrates is of particular interest. Indeed, carbon is highly conductive, relatively stable and cheap. Furthermore, it was reported that nanoparticles sometimes have higher catalytic properties than the corresponding bulk material [6]. The electroless deposition of metallic nanoparticles on glassy carbon microspheres was achieved recently [7-9]. However, poor control of the size and spreading of the nanoparticles was obtained. Specific efforts led us, here, to obtain, for the first time, well-defined and well-spread platinum nanoparticles (PtNPs) of  $100 \pm 40$  nm on carbon microspheres. The catalytic properties of the resulting material were demonstrated by electrochemical studies. In some cases specific substrates are electroactive only at specific electrode materials. In the case where the metallic nanoparticles are electroactive towards the considered substrate but the carbon support is inactive, the nanoparticle array can be considered as a nanoelectrode array. The nanoparticle arrays were used for the development of a low cost practical Pt nanoelectrode array sensor for proton detection. In addition, methanol oxidation was studied to exemplify potential use in fuel cells. The procedures described are very simple to apply and represent an original strategy for the development of catalytic surfaces in general.

## 2. EXPERIMENTAL PART

### 2.1. Chemicals and Materials

Hydrochloric acid (37 wt. % solution in water) and methanol (99.99 %) were supplied from Riedel-de Häen. Potassium chloride (KCl, 99.5 %), L-ascorbic acid, hexachloroplatinate ( $\text{H}_2\text{PtCl}_6$ , 98 %) and sodium hydroxide (99.5 %) were obtained from Sigma-Aldrich and used without further purification. Glassy carbon spherical powder (10–20 microns, type 1) was purchased from Alfa Aesar (Heysham, UK). The deionised water used had a resistivity not less than  $18.2 \text{ M}\Omega \text{ cm}$  at  $25 \text{ }^\circ\text{C}$  (Vivendi Water Systems, UK). As far as the KCl electrolyte solutions are concerned, their pH was brought to  $7 \pm 0.3$  prior to HCl additions.

### 2.2. Electroless deposition of platinum nanoparticles on glassy carbon microspheres

The synthesis of platinum nanoparticles on glassy carbon microspheres was done as described below. 100 mg of glassy carbon microspheres were suspended in 50 mL of water. The glassy carbon microspheres were used as received and were not further purified nor activated. 20 mg of platinum

hexachloroplatinate and 46 mg of L-ascorbic acid were added to the solution under vigorous stirring at 70 °C. The pH of the reaction medium was then adjusted to 5.2 using a 1 M sodium hydroxide solution. The reaction flask was wrapped in aluminum foil and the reaction was allowed to proceed for two hours at 70 °C under stirring.

### 2.3. Abrasive attachment of carbon microspheres

The abrasive attachment of glassy carbon microspheres on a basal plane pyrolytic graphite electrode was done by rubbing the electrode surface onto a thin layer of microspheres powder laying on a filter paper. The excess of non attached microspheres on the electrode surface is then removed by the process of rubbing the electrode in a wet cotton cloth. The electrode surface can be renewed before modification by pressing cellotape on the electrode surface and removing it along with several surface layers of graphite.

### 2.4. Instrumentation

The electrochemical cell was a standard three electrode cell. Except when specified otherwise, the reference electrode was an aqueous saturated calomel electrode (Radiometer Analytical) and the auxiliary electrode was a carbon graphite rod. The working macrodisc electrode was a 5 mm diameter basal plane pyrolytic graphite electrode (BPPG, Le Carbone Ltd, Sussex, UK). All experiments were performed at room temperature under an argon atmosphere. The electrochemical investigations were performed using an Eco Chemie PGSTAT20 potentiostat connected to a computer. Scanning electron microscopy (SEM) imaging of the decorated carbon microspheres was carried out using a JEOL JSM model 6300F scanning electron microscope.

### 2.5. Modelling

The model used in this paper for simulating the peak currents obtained at random nanoparticle arrays or macroparticle arrays was described and discussed in detail in a previous work [10]. The model considers the electron transfer to occur at the surface of a spherical particle supported by an electro-inactive planar surface. The mass transport equation for the electroactive species is solved by finite difference methods. The diffusion domain approximation [11] is used to model a randomly distributed array of the spheres on the electrode surface. It is assumed that the electron transfer is fast and reversible and that both the reactant and product of the electron transfer are soluble and have equal diffusion coefficients. We note the limitations of these assumptions in describing the mechanism of the reduction of protons on platinum; however the variation of peak current with particle coverage is likely to be predicted to a good approximation.

### 2.6. Limit of detection

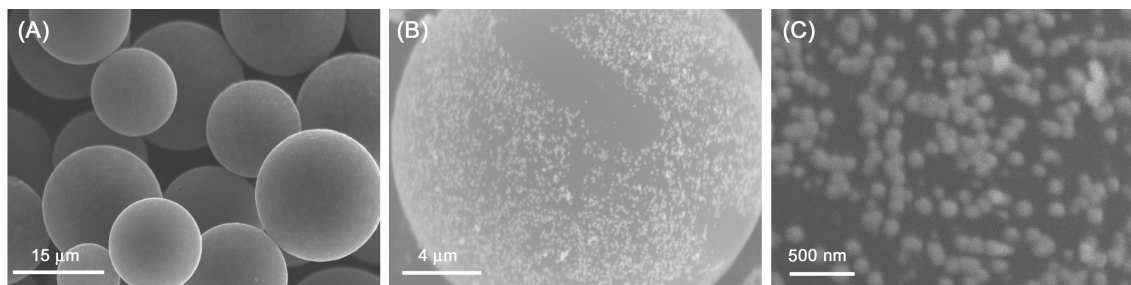
The given values correspond to limits of detection reachable with a standard addition method consisting in 5 additions of 200  $\mu\text{M}$  HCl to the sample. Experimentally, the calculation is based on the peak current values obtained for voltammetric scans at 0.1  $\text{V s}^{-1}$  in 0.1 M KCl.

*Diffusion coefficients:* The diffusion coefficients for the proton and the ferrocyanide ions that were used for the simulations and for the Randles-Ševčík plots were respectively  $7.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $0.76 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  [12,13].

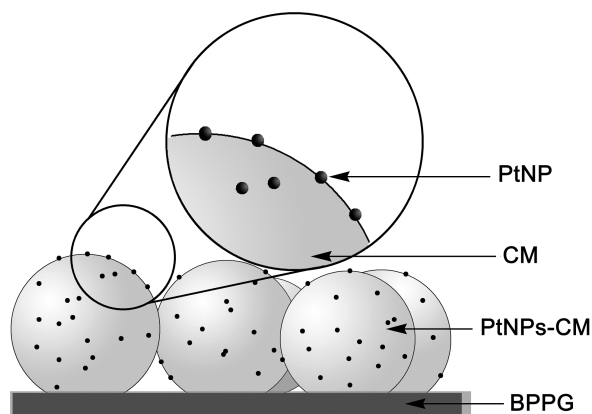
### 3. RESULTS AND DISCUSSION

#### 3.1. Preparation and characterization of PtNPs arrays

A new method for the synthesis of Pt nanoparticles on glassy carbon microspheres was developed using ascorbic acid as the reducing agent. The method is very simple and easy to perform (see experimental section). The glassy carbon microspheres with a diameter of  $15 \pm 5 \mu\text{m}$  (Fig. 1(A)) were used as the carbon support. From the SEM images of the PtNPs obtained (Fig. 1(B) and Fig. 1(C)) it can be observed that most of the PtNPs have a diameter of  $100 \pm 40 \text{ nm}$  and that they are relatively well spread on the surface of the carbon microspheres with an interparticle distance of about 0 to 220 nm. Furthermore the nature of the PtNPs was confirmed by Energy Dispersive X-ray Analysis (EDX).

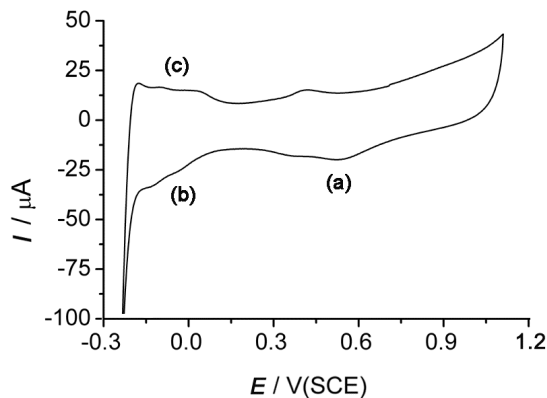


**Figure 1.** SEM images of (A) non-modified glassy carbon microspheres (CMs), (B) and (C) platinum nanoparticles on glassy carbon microspheres (PtNPs-CMs).



**Scheme 1.** Schematic representation of the platinum nanoparticle array on a BPPG electrode surface.

Glassy carbon microspheres can be abrasively attached to a basal plane pyrolytic graphite electrode surface by a very quick, simple and easy procedure [8]. Indeed, it takes a few minutes to get a nanoparticle array and it is expected that the method does not produce agglomerates of nanoparticles. A schematic representation of the electrode architecture obtained is presented in Scheme 1.



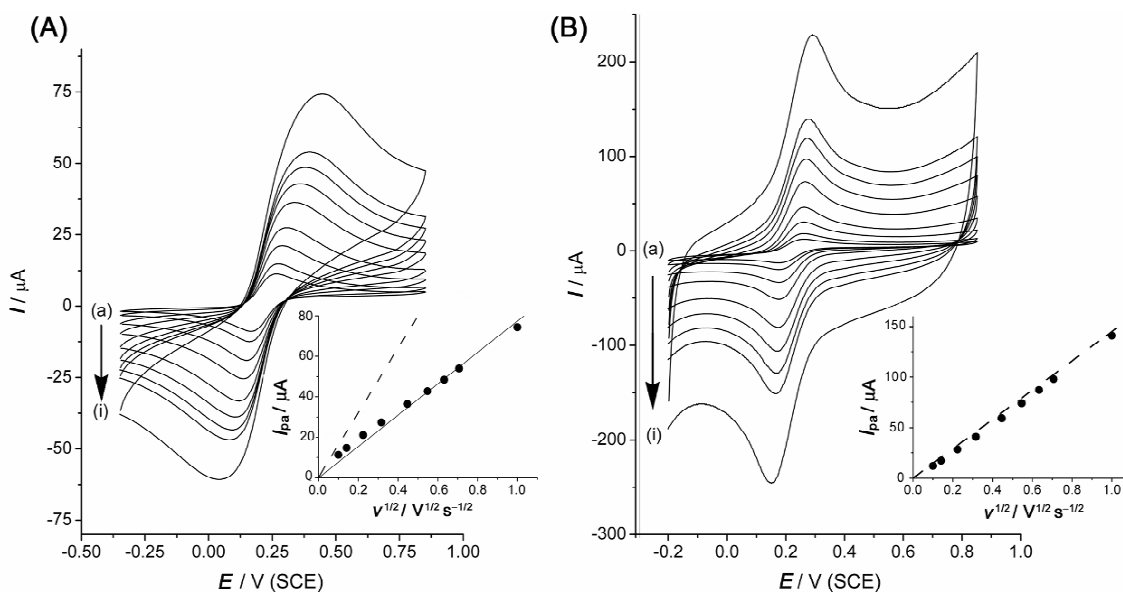
**Figure 2.** Cyclic voltammetry of a 5 mm diameter platinum nanoparticle array in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 100 mV s<sup>-1</sup>.

The modified electrode consisting in a platinum nanoparticle array on a carbon matrix was used in all the following studies presented in this work. Fig. 2 corresponds to a cyclic voltammetry experiment run in 0.5 M H<sub>2</sub>SO<sub>4</sub> at the modified electrode obtained by the above described procedure. The voltammogram obtained presents the characteristic features of platinum material electrodes. Indeed, in the course of a voltammetric scan an oxidation is observed, and in the backward scan the peaks observed at about 0.5 V (a) and -0.1 *versus* SCE (b) respectively correspond to the reduction of platinum oxides and the adsorption of hydrogen. Moreover, the peak (c) observed after reversing the scan direction once again is characteristic of the hydrogen desorption. From the voltammogram of Fig. 2, it can then be concluded that the Pt particles are present on the electrode surface and that they are electrically connected to the electrode. Furthermore, the integration of the hydrogen adsorption peaks could be used to estimate the total surface coverage of the platinum [14]. Using this method and a value of 208 μC cm<sup>-2</sup>, a total surface area of 0.123 cm<sup>2</sup> was estimated for the modified electrode used in Fig. 2. It is worth emphasizing that for this experiment a platinum wire was used as the reference electrode instead of the SCE so as to avoid the transfer of chloride ions in the electrolyte. Once the cyclic voltammogram was recorded a further recording was made using the SCE electrode so as to get the peak potentials *versus* SCE. Such precautions have to be taken so as to get a viable estimation of the platinum surface from the integration of the peaks that correspond the hydrogen adsorption [14].

### 3.2. Cyclic voltammetry at PtNPs arrays

The PtNPs array obtained was also tested for the oxidation of ferrocyanide. As it can be observed in Fig. 3 the ferrocyanide/ferricyanide couple has a well defined reversible electrochemical

behaviour both at a non-modified basal plane pyrolytic electrode (BPPG) electrode (Fig. 3(A)) and at a BPPG modified with PtNPs (Fig. 3(B)). A closer look, however, shows that the peak to peak separation at  $100 \text{ mV s}^{-1}$  is 0.180 and 0.085 V respectively at the non-modified and at the modified BPPG. The large value obtained at the non-modified BPPG electrode has been recently attributed to the decrease of the electron transfer kinetics due to the oxygenation of the edge plane sites [15]. It is interesting to see, here, that the immobilisation of platinum nanoparticles on glassy carbon microspheres (PtNPs-CMs) on the BPPG electrode surface restores fast electron transfer kinetics. In that case the measured current corresponds to the addition of the current obtained at the PtNPs-CMs and of the current obtained at the BPPG surface. The plots of the peak current versus square root of the scan rate (Insets Fig. 3) show that at the modified BPPG electrode the current almost matches with the current calculated using the Randles-Ševčík formula. It then can be said that the BPPG electrodes modified with PtNPs-CMs behave as macrodisc electrodes in voltammetry.

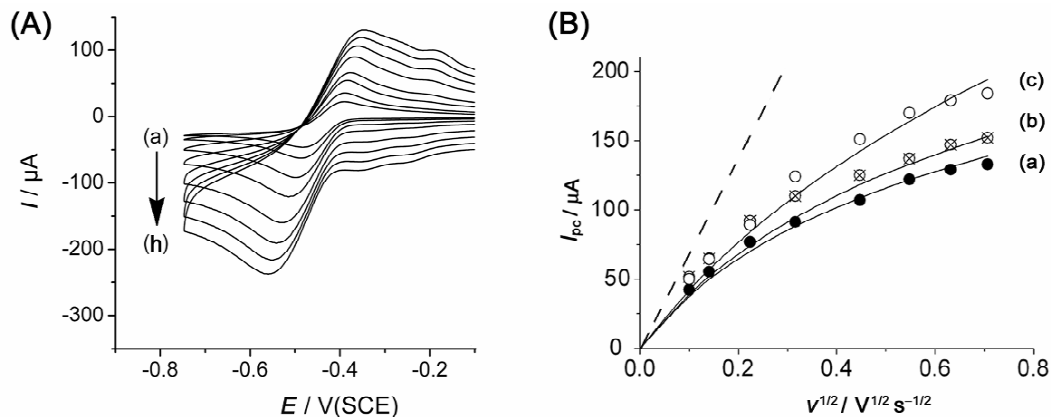


**Figure 3.** Cyclic voltammetry of 1 mM potassium ferrocyanide and 0.1 M KCl, (A) at a 5 mm diameter BPPG electrode (B) at a 5 mm diameter BPPG electrode modified with glassy carbon microspheres decorated with platinum nanoparticles (PtNPs-CMs) (total PtNPs loading of  $0.100 \text{ cm}^2$ ). The voltammograms were recorded at (a) 10, (b) 20, (c) 50, (d) 100, (e) 200, (f) 300, (g) 400, (h) 500 and (i)  $1000 \text{ mV s}^{-1}$ . Insets: plot of  $I_{pa}$  versus  $v^{1/2}$ . Dashed line: expected plot using the Randles-Ševčík formula.

### 3.3. Proton reduction at PtNPs arrays

The PtNPs arrays were then used for the proton reduction. As far as the proton reduction is concerned no electroactivity was observed in the range of potentials explored at a BPPG electrode or a BPPG electrode modified with carbon microspheres (CMs). The voltammograms obtained at a BPPG electrode modified with PtNPs-CMs and at various scan rates are shown in Fig. 4(A). Well defined reversible peaks are obtained. The electrode reaction mechanism involves the transfer of one electron

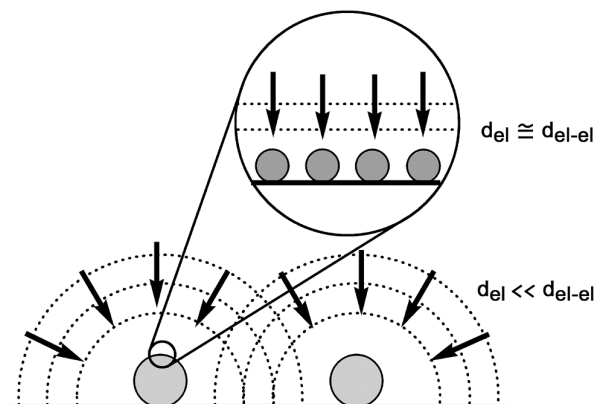
per proton ( $H^+$ ), the neutral hydrogen atom is adsorbed ( $H_{ad}$ ) on the platinum surface. The plot of the peak current versus the square root of the scan rate for three different PtNPs loadings is given Fig. 4(B). The lower the density of PtNPs is, the more the plot deviates further from the Randles-Ševčík calculated line.



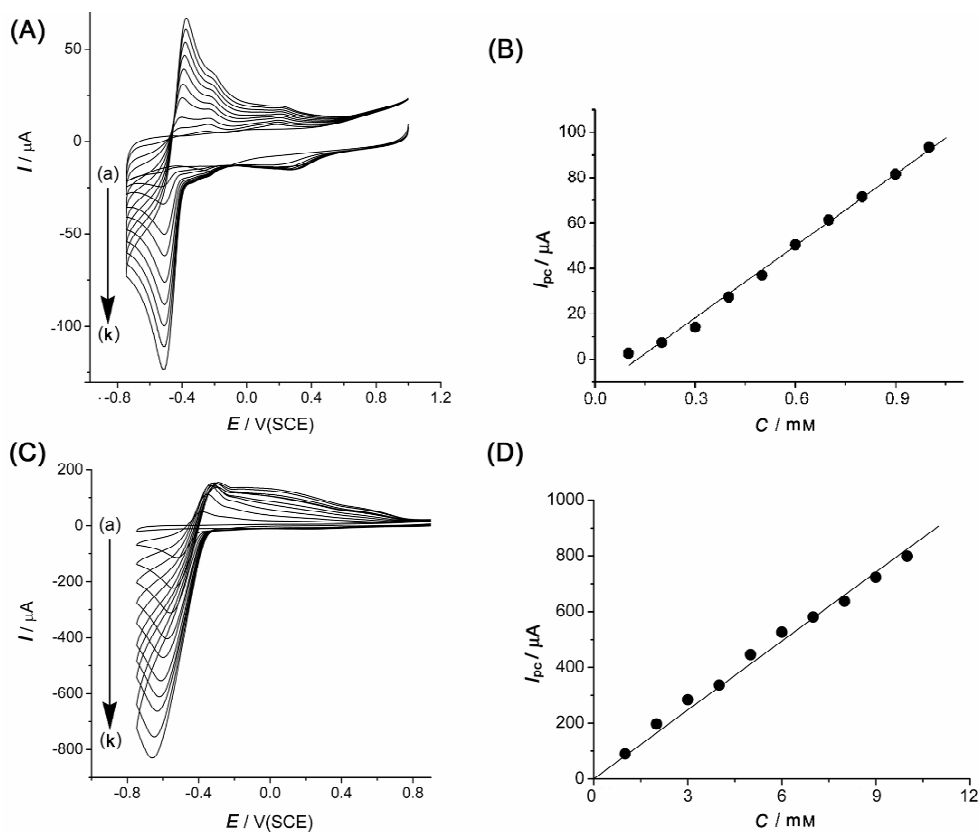
**Figure 4.** (A) Cyclic voltammetry at a 5 mm diameter platinum nanoparticle array (total PtNPs loading of  $0.123 \text{ cm}^2$ ) in 1 mM HCl and 0.1 M KCl at (a) 10, (b) 20, (c) 50, (d) 100, (e) 200, (f) 300, (g) 400, (h)  $500 \text{ mV s}^{-1}$ . (B) Plot of  $I_{pc}$  versus  $v^{1/2}$  for various total platinum loadings (a),  $0.123$  (b)  $0.186$  and (c)  $0.196 \text{ cm}^2$ ; the points and the curves correspond respectively to the experimental and the modelled peak currents. Dashed line: expected plot using the Randles-Ševčík formula.

Recently, a theoretical study performed in our laboratory showed that the voltammetry at isolated nanoparticles or microparticles [16] and at nanoparticles or microparticles random arrays [10] can be efficiently modelled. The diffusion domain approach was used for the modelling of the diffusional current at random arrays. In our electrode configuration, it is convenient to distinguish the nanoparticles on the carbon microspheres in one hand and in the other hand the decorated microspheres on the BPPG electrode surface. As far as the PtNPs on the carbon microspheres are concerned their diameter size ( $100 \pm 40 \text{ nm}$ ) and their interparticle distance ( $0 - 220 \text{ nm}$ ) were determined by SEM. Using these values the modelling shows that the corresponding diffusion domains heavily overlap and the whole is equivalent to a linear diffusion. That is to say the carbon microsphere decorated with this density of nanoparticles will behave exactly like if the carbon microsphere was completely covered by a smooth layer of platinum. This case of mass transport has been classified in previous works as category 4 [10,17]. As far as the microspheres on the BPPG surface are concerned, the currents obtained shows that their density is enough to have their diffusion domains overlapping but that they do not overlap completely. This situation was previously classified as category 3 [10,17]. A schematic representation of the diffusion both at a decorated carbon microsphere surface and at the modified-BPPG surface is given in Scheme 2. A full modelling of the peak currents was performed and it can be seen from Fig 4(B) that a reasonable fitting of the experimental data was obtained. The modeling allowed us to estimate the number of decorated microspheres that are present on the whole BPPG electrode surface. For the modified electrodes used in Fig. 4(B) curves a), b) and c) the number

of microspheres immobilized on the whole electrode surface was estimated to be respectively 2900, 3289 and 4621.



**Scheme 2.** Schematic representation of the diffusion zones at spherical nanoparticles (PtNPs diameter  $\leq$  distance between PtNPs) on microspheres (CMs diameter  $\ll$  distance between CMs) on a supporting planar surface.



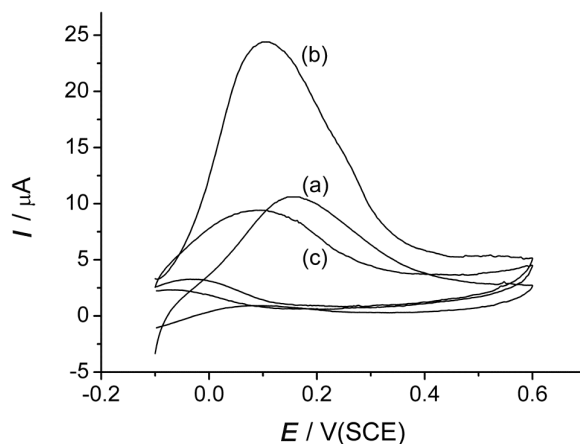
**Figure 5.** Cyclic voltammetry at a 5 mm diameter platinum nanoparticle array (total PtNPs loading of  $0.123 \text{ cm}^2$ ) in  $0.1 \text{ M KCl}$  at  $100 \text{ mV s}^{-1}$  for various concentrations of  $\text{HCl}$ ; (A) (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5, (g) 0.6, (h) 0.7, (i) 0.8, (j) 0.9, (k) 1 mM; (C) (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, (f) 5, (g) 6, (h) 7, (i) 8, (j) 9, (k) 10 mM; (B) and (D) are the corresponding calibration curves.



The use of the BPPG electrode modified with PtNPs-CMs for the accurate determination of the pH was then explored. Fig. 5(A) and Fig. 5(C) show the voltammetric response obtained at  $100 \text{ mV s}^{-1}$ , respectively, for 0.1 and 1 mM additions; and the corresponding calibration curves are presented, respectively, in Fig. 5(B) and Fig. 5(D). A sensitivity of  $0.46 \text{ mA mol}^{-1} \text{ cm}$  and a detection limit of  $200 \text{ }\mu\text{M}$  were obtained. The peak current increases linearly for concentrations between 0.1 mM and 10 mM. It is then possible, using this method, to get precise pH measurements within the range  $\text{pH} = 1\text{--}3$ .

### 3.4. Methanol oxidation at PtNPs arrays

A further study involved the use of the PtNPs arrays for methanol oxidation in alkaline solution to exemplify their potential use in fuel cells. The cyclic voltammograms obtained are presented Fig. 6. At a non-modified BPPG electrode or at a BPPG electrode modified with CMs, and in the range of potentials considered, no oxidation current was observed. However at a BPPG electrode modified with PtNPs-CMs a large oxidation peak was recorded. It was shown, however, that the electrode gets poisoned very quickly (less than half of the current remained after two cycles). This observation is in good agreement with previous methanol oxidation studies at PtNPs [18].



**Figure 6.** Cyclic voltammetry at a 5 mm diameter platinum nanoparticle array (total PtNPs loading of  $0.340 \text{ cm}^2$ ) at  $5 \text{ mV s}^{-1}$  in 1 M KOH and methanol (a) 0.5 M, (b) 1 M (1<sup>st</sup> cycle) and (c) 1 M (2<sup>nd</sup> cycle).

## 4. CONCLUSIONS

The construction of well-defined catalytic surfaces on a carbon matrix support, using the abrasive attachment of glassy carbon microspheres decorated with platinum nanoparticles on BPPG electrodes, is presented. It was shown that the platinum nanoparticle arrays obtained behaves as a macrodisc electrode for species that are electroactive at carbon and platinum materials (*i.e.* ferrocyanide). While for species that are electroactive at platinum materials but not at carbon materials (*i.e.*  $\text{H}^+$ , methanol) it acts as a nanoelectrode array. It can be stressed out that the abrasive attachment

of the modified microspheres is a very quick and efficient way to obtain platinum nanoparticle arrays. Moreover, it is believed that the method presented can be generalized to nanoelectrode arrays of other metals provided that the synthesis of metallic nanoparticles on carbon microspheres is obtained. In addition, the electrode architecture presented was found to have excellent characteristics as for the sensing of protons and might be used as an original strategy for the precise determination of pH for values between 1 and 3.

#### ACKNOWLEDGEMENTS

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