Carbon-stabilized porous silicon as novel voltammetric sensor platforms

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ABSTRACT

The use of carbon-stabilized porous silicon (pSi) as a voltammetric sensing platform able to discriminate the detection of various electroactive species with similar redox potentials is demonstrated for the first time. For this purpose, the voltammetric responses to the presence of the three dihydroxybenzene isomers hydroquinone, catechol and resorcinol were studied using thermally hydrocarbonized pSi (THCpSi) and thermally carbonized

pSi (TCpSi), as well as a glassy carbon electrode (GCE) as a benchmark. Both THCpSi and TCpSi outperformed the electrochemical performance of a GCE, as shown by the electrochemical characterization performed in the presence of the redox pair $[Fe(CN)_6]^{3-/4-}$. Cyclic voltammetry results demonstrated that both THCpSi and TCpSi exhibited fast electron transfer kinetics, with TCpSi showing a slightly improved electrochemical performance. The electrode catalytic enhancement shown by these carbon-stabilized nanostructures was harnessed to allow the simultaneous voltammetric determination of hydroquinone, catechol and resorcinol. The analytical performance of TCpSi to the detection of the three dihydroxybenzene isomers was studied using differential pulse voltammetry, revealing good reproducibility, high sensitivity, low limits of detection (all below 5 µmol L^{-1}) and good recoveries (between 98% and 102%) in the analysis of spiked tap water samples.

Keywords: Porous silicon; carbon stabilization; electrochemical sensor; differential pulse voltammetry; dihydroxybenzene isomers

1. INTRODUCTION

Porous silicon (pSi) is a versatile porous semiconductor that has attracted attention in a wide range of fields with applications as diverse as drug delivery, energy conversion and sensing, among others. This wide interest is due to some of the unique features of pSi such as its availability, biocompatibility, fast and simple fabrication process, large surface area, adjustable pore size, thickness and porosity, and a convenient surface chemistry that allows different routes for functionalization [1–3].

In particular, the possibility to control the pore morphology of pSi and its versatile surface chemistry provide a wide range of options to design chemical sensors and biosensors. In

fact, pSi has been successfully applied to the development of optical and electrical sensors. Optical sensors are commonly based on monitoring the shift in the interferometric reflectance fringe pattern caused by changes in the average refractive index [4], whereas electrical sensors usually rely on measuring either conductance or capacitance changes [4]. However, little research has been done on the development of electrochemical sensors based on pSi, which present some interesting features including high sensitivity, low cost, relatively simple instrumentation, easy miniaturization and portability [5,6]. To the best of our knowledge, the coupling of pSi with electrochemical sensing has mainly been studied in the form of amperometric and impedimetric biosensors [7], without further exploring the possibilities of non-functionalized voltammetric pSi sensors.

While pSi presents as a promising electrochemical transducer, one of the main challenges faced is the low chemical stability of freshly etched pSi. Highly reactive silicon hydride species present can easily be oxidized in both water and air resulting in the formation of an insulating SiO_2 layer. Stabilization methods based on pSi oxidation through thermal, chemical or anodic oxidation treatments promote the growth of the insulating SiO_2 layer which limits the performance of certain electrochemical transduction techniques. Other approaches that have been explored to both stabilize and modify the electrical properties of pSi, making it more fit for electrochemical sensing, include various thin film coating methods based on metals or conductive polymers [4].

Another method that allows the stabilization of pSi is based on the introduction all over its contour of an ultrathin, conformal carbon layer by thermal decomposition of acetylene. This method was first introduced by Salonen *et al.* [5] and has already found many applications in the fields of drug delivery, optical sensors, batteries and electrochemical supercapacitors [6,8]. However, it was only recently that this stabilization method was

explored for the development of electrochemical sensors. Guo *et al.* [9] studied the electrochemical performance of thermally hydrocarbonized pSi (THCpSi) and thermally carbonized pSi (TCpSi) and demonstrated that carbon-stabilized pSi presents fast electron transfer kinetics while maintaining the unique features of pSi (large surface area, adjustable pore morphology, versatile surface chemistry…), rendering it suitable as electrochemical platform. The development of an impedimetric immunosensor for the detection of MS2 bacteriophage based on an anti-MS2 antibody-modified THCpSi platform was reported, highlighting the potential of carbon-stabilized pSi for biosensing applications.

Carbon-stabilized pSi presents some interesting features derived from the ultrathin carbon layer formed during the thermal decomposition of acetylene that can be exploited to widen its application to voltammetric chemical sensors with unique advantages. It has been shown that the coupling of carbon-based nanomaterials with electrochemical sensors not only increases their sensitivity but can also provide a better selectivity towards some analytes [10,11]. Carbon-stabilized pSi is not just appealing to biosensing applications; it can also be a good electrochemical platform as a bare substrate, without the need of further modification, therefore constituting a clear advantage over other carbon-based nanomaterials sensors.

Thus, in this work we report for the first time the application of non-functionalized carbon-stabilized pSi in electrochemical sensing. For this purpose, the electrochemical performance of both THCpSi and TCpSi was investigated via differential pulse voltammetry (DPV) measurements to determine three dihydroxybenzene isomers, namely catechol (CC), hydroquinone (HQ) and resorcinol (RC), commonly used as chemicals in several products (e.g., cosmetics, dyes, pesticides, medicines) and considered to be environmental pollutants due to their high toxicity and low degradability

[12,13]. The presence of CC, HQ and RC has been reported in effluents from various industries (e.g. textile, pharmaceutical, plastic) and in the wastewater of synthetic coal fuel conversion processes with concentrations ranging from 9 μmol L^{-1} to 9 mmol L^{-1} [14]. The direct simultaneous voltammetric determination of these three isomers is usually problematic due to the close oxidation potential of HQ and CC. To tackle this difficult problem without resorting to sample treatment, two main approaches can be followed: (i) signal deconvolution by means of chemometric treatments or (ii) improvement of the working electrode catalytic response through its modification. Regarding the former approach, there have been some attempts allowing the voltammetric determination of such compounds using various chemometric strategies [15–17]. In the latter approach, the incorporation of several nanomaterials has been reported to enlarge the separation of HQ and CC voltammetric peaks. In particular, good results have been achieved by modifying the working electrode with graphene [16,18,19], carbon nanotubes [11,20,21], mesoporous materials [22,23] and their combination with metal nanoparticles [24–26], among others. In this work, catalytic enhancement is achieved through the ultrathin carbon layer generated during carbon-stabilization of pSi, allowing a good discrimination among HQ, CC and RC.

2. MATERIALS AND METHODS

2.1. Materials

6-inch, boron doped (p-type) Si wafers with 0.00055-0.001 Ω cm resistivity, (100)-oriented were purchased from Siltronix (France). Hydrofluoric acid (HF, 48%, AR grade) was purchased from Scharlau (Australia). The acetylene gas cylinder (industrial grade, dissolved) was purchased from BOC (Australia). Potassium ferricyanide $K_3[Fe(CN)_6]$,

potassium ferrocyanide $K_4[Fe(CN)_6]$, HQ, CC, RC and phosphate buffered saline (PBS) tablets were provided by Sigma-Aldrich (Australia).

2.2. Instrumentation

Scanning electron microscopy (SEM) images were obtained with a FEI NovaNano SEM 430 at an accelerating voltage of 10 kV. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed with a Thermo Scientific Nicolet 6700 FTIR spectrometer. Raman spectra were acquired using a Renishaw inVia Raman microscope with a 100 mW 532 nm laser excitation source. A 10% excitation power density was applied to avoid damage of the surface.

Electrochemical measurements were performed on a CH Instrument model 600D Series (CH Instruments, USA) controlled with the provided software package. A homemade three-electrode Teflon cell placed in a Faraday cage, and containing the THCpSi or TCpSi substrate as the working electrode, was used. The working electrode area was delimited to 7.5 mm diameter by an O-ring. A Ag/AgCl/NaCl (3 mol L^{-1}) electrode provided by BAS Inc (West Lafayette, IN, USA) and a platinum wire were used as reference and counter electrodes, respectively. Glassy carbon electrodes (GCE) with 3 mm diameter used for comparison purposes were provided by CH Instruments. All the potentials are referred to Ag/AgCl.

2.3. Fabrication of THCpSi and TCpSi

2.3.1. Fabrication of pSi

A 6-inch Si wafer was anodically etched in an electrolyte solution containing 1:1 (v:v) HF/ethanol to produce pSi, using a MPSB wet etching system (A.M.M.T GmbH, Germany), which exposes an etching area of 132 cm^2. A sacrificial layer produced with a current density of 61 mA cm^{-2} for 30 s was removed with 1 mol L^{-1} sodium hydroxide

[27]. Then the etching cell was rinsed with water, absolute ethanol and dried with N_2 gas. Next, a current density of 53 mA cm^{-2} was applied to the etching cell for either 20 s or 60 s to form a porous film with pores of 72 ± 15 nm in diameter and a thickness of 500 nm or 1.5 µm, respectively. The freshly etched pSi was finally rinsed with ethanol and dried with N_2 gas to immediately proceed with its carbon stabilization. The thin film of pSi was used for sensing purposes, while the thick layer of pSi was used to perform FTIR and Raman measurements.

2.3.2. Carbon stabilization of pSi by thermal decomposition of acetylene gas

Thermal hydrocarbonization of freshly etched pSi (THCpSi) was carried out at 525 ºC under a 1:1 N_2:acetylene mixture flow, whereas thermal carbonization of freshly etched pSi (TCpSi) consisted on a two-step carbonization process, where THC treatment was followed by annealing at 800 ºC. More detailed experimental information can be found elsewhere [9].

2.4. Measurement of interferometric reflectance spectra

Interferometric reflectance Fourier Transform spectroscopy was used to study the stability of pSi, THCpSi and TCpSi. Interferometric reflectance spectra were obtained using a tungsten lamp (Ocean Optics) and a CCD spectrometer (Ocean Optics S- 2000). Incident light was fed through one end of a bifurcated fiber optic cable and focused through a lens onto the porous films. Reflected light from the porous film was collected through the same optical lens and transferred to the CCD spectrometer via the second arm of the bifurcated optic cable. For reflectance measurements, the spectra were referenced to a silver mirror. Reflectivity spectra were recorded in the wavelength range 350–1100 nm, with a spectral acquisition time of 20 ms. Igor program library was applied to the

resulting spectra to provide a single peak which position corresponds to the effective optical thickness (EOT). EOT monitoring provided information about the stability of the various pSi samples tested.

2.5. Electrochemical measurements

Electrochemical characterization was performed by cyclic voltammetry (CV) using 2 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ in 10 mmol L^{-1} PBS buffer (pH 7.4) as redox probe. CV measurements were performed from -0.2 to 0.8 V at a scan rate of 100 mV s^{-1}.

To assess the analytical performance of the various pSi substrates towards the electrochemical detection of the three dihydroxybenzene isomers, CC, HQ and RC, solutions of each one of those compounds were prepared daily in deaerated 10 mmol L^{-1} PBS buffer (pH 7.4) and kept in the dark to prevent oxidation. CV measurements were performed between -0.3 and 1 V at a scan rate of 50 mV s^{-1} and DPV measurements were performed after 30 s stirring by scanning the potential from -0.2 to 0.9 V using step potentials of 5 mV, pulse amplitudes of 50 mV and pulse times of 50 ms.

Tap water samples were collected in December 2019 from the local distribution network in Barcelona, managed by Agbar Company and mostly using water coming from Llobregat River. The collected samples were spiked with HQ and CC to a final concentration of 5.8 µmol L^{-1} of each isomer, and pH was adjusted to 7.4 (dilution ratio 2:1). DPV measurements were carried out using the above-mentioned conditions without any further sample treatment. In addition, non-spiked tap water was scanned to confirm the absence of the target analytes.

3. RESULTS AND DISCUSSION

3.1. THCpSi and TCpSi fabrication and characterization

Carbon stabilization by thermal treatment of pSi in the presence of acetylene was used to stabilize pSi samples. As it was previously reported by Guo *et al.* [9], this procedure allows stabilizing pSi without altering its nanostructured morphology, which can be controlled by adjusting the anodization conditions. Both THCpSi and TCpSi retain the morphological features of as-prepared pSi. **Figure 1** shows the SEM images obtained for TCpSi nanostructures, with an average pore diameter of 72 ± 15 nm and 500 nm thickness. TCpSi was chosen as potential voltammetric sensing platform for this study due to its excellent electrochemical properties which are later discussed.

FTIR and Raman spectroscopy were used to characterize the chemical composition of freshly etched pSi, THCpSi and TCpSi. As shown by the FTIR spectra in **Figure 2a**, after both thermal treatments, the characteristic bands of freshly etched pSi at 2087, 2114 and 905 cm^{-1}, corresponding to the stretching vibrations of Si-H and $Si-H_2$ and the Si-H deformation mode, respectively, completely disappeared and were substituted by new bands associated to saturated C-H at 2920 and 3047 cm^{-1}, unsaturated C=C stretching vibrations at 1592 cm^{-1}, and the CH_3 symmetric deformation mode of $Si-CH_3$ at 1270 cm^{-1}. Raman spectroscopy was used to confirm the successful carbonization of pSi, shown in **Figure 2b** by the peaks depicted for both THCpSi and TCpSi at 1350 (D band) and 1580 cm^{-1} (G band), which are Raman signatures for carbon materials [28]. Furthermore, both THCpSi and TCpSi preserved the crystallinity of Si after carbon-stabilization, as shown by the Si lattice mode at 515 cm^{-1}.

The chemical stability of pSi, THCpSi and TCpSi was investigated by recording the interferometric reflectance spectra obtained after exposure to 10 mM PBS buffer at pH 7.4. Both THCpSi and TCpSi single layers retain the Fabry-Pérot fringe pattern characteristic of pSi, although with a lower intensity. The fringe maximum follows the Fabry-Pérot relationship [27]:

$$m\lambda = 2nL \quad (1)$$

where m is an integer corresponding to the spectral order of the fringe, λ is the wavelength of incident light, n is the average refractive index of the porous matrix, and L is the physical thickness of the porous layer. The EOT referring to the 2nL is determined from the Fourier transform of the reflectance spectrum (**Figure 3a**). The pSi, THCpSi and TCpSi samples were incubated in PBS buffer for 15, 30, 45, 60, 105 and 180 min, washed with milliQ water and dried, before the optical spectra were recorded. The relative percentage change in EOT (ΔEOT%) was calculated as previously reported [29]:

$$\Delta EOT\% = (nL - nL_0) / nL_0 \times 100 \quad (2)$$

where nL_0 is the value measured just before exposing the sample to buffer. **Figure 3b** shows the ΔEOT% as a function of the time exposed to PBS. The decrease in EOT observed is indicative of the degradation and subsequent dissolution of the pSi surface. While non-stabilized pSi significantly degrades over time as shown by the constant decrease in EOT after incubation in PBS, both THCpSi and TCpSi show negligible decrease in EOT (< 1%) over an incubation time of 180 min. These results underpin the chemical stability of both carbon-stabilized nanostructures.

The electrochemical performance of both THCpSi and TCpSi was evaluated by CV in the presence of 2 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ in 10 mmol L^{-1} PBS buffer (pH 7.4) as redox probe. **Figure 4a** shows the CV measurements of 20 consecutive cycles for THCpSi and TCpSi samples, while **Figure 4b** shows triplicates of the nineteenth scan for both samples. The peak current and peak potential separation values extracted from the CVs in Figure 4b are summarized in **Table 1**. THCpSi and TCpSi depict well-defined $[Fe(CN)_6]^{3-/4-}$ redox peaks, TCpSi showing a slightly improved electrochemical performance, inferred by the larger current intensity values and smaller peak-to-peak

potential difference this carbon-stabilized substrate exhibits. Both THCpSi and TCpSi samples show a highly stable response along 20 consecutive measurements, with a relative standard deviation (RSD) associated to the oxidation peak current of 0.5% and 0.2%, respectively, supporting their excellent response repeatability. The reproducibility among electrodes prepared from three rounds of TC and THC treatments conducted separately using the same batch of pSi samples was also outstanding, with RSD values for the oxidation peak current of 0.8% and 1.8%, respectively. The slightly better electrochemical performance observed for TCpSi might be attributed to its improved chemical stability and higher carbon surface coverage [9].

3.2. Electrochemical behavior of HQ, CC and RC

Initially the electrochemical behavior of HQ, CC and RC prepared in PBS at pH 7.4 was studied by CV using both TCpSi and THCpSi as working electrodes, and compared to the behavior observed using a GCE. **Figure 5** shows the cyclic voltammograms obtained for a solution containing 30 µmol L^{-1} of either HQ, CC or RC, using each sensor.

As it can be seen, both HQ (**Figure 5a**) and CC (**Figure 5b**) present a similar behavior using GCE, with an anodic and a cathodic peak, at 341 and -103 mV for HQ, and at 403 and 19 mV for CC, respectively. This corresponds to a peak potential separation (ΔE_p) of 444 and 384 mV for HQ and CC, respectively, which differs significantly from the 29.5 mV characteristic of the two-electron reactions expected in this case (**Figure 6**), indicating that both HQ and CC present an irreversible electrochemical behavior at GCE. On the other hand, much higher currents were achieved with both TCpSi and THCpSi, which can be attributed to their larger surface area. However, in terms of reversibility TCpSi showed a much better behavior, reducing the ΔE_p to 47 and 18 mV for HQ and CC, respectively, which is probably due to the improved electron transfer kinetics

provided by the carbon-stabilized pSi. The lack of improvement in reversibility observed in the case of THCpSi (ΔE_p for HQ and CC are 650 mV and 341 mV, respectively) could be explained by its hydrophobic nature, which hinders the interaction with dihydroxybenzene isomers through hydrogen bonds [30]. As previously reported by Guo *et al.,* THCpSi features a hydrophobic surface with an estimated water contact angle above 120°, while TCpSi presents a hydrophilic surface with a low water contact angle of approximately 30° [9].

The electrochemical behavior of RC (**Figure 5c**) is completely different from that shown by HQ and CC. No cathodic peak was observed at GCE and the anodic current was much smaller than those of HQ and CC. These facts could be attributed to the low thermodynamic stability of the RC quinonic form and the lack of aromatic ring activation due to the OH groups at meta- position [31]. Regarding the carbon-stabilized pSi substrates, the RC anodic peak was only observed in the case of TCpSi, where it was shifted to less positive potentials.

Considering these results and in particular both the slightly better stability shown in the CV characterization with $[Fe(CN)_6]^{3-/4-}$ and the improved electron transfer kinetics that gives rise to a more reversible behavior of HQ and CC, TCpSi was selected as the best carbon-stabilized pSi substrate for voltammetric chemical sensing and considered for further studies.

In this sense, its applicability to the simultaneous determination of HQ, CC and RC was evaluated by DPV. **Figure 7** shows the representative voltammograms obtained for a solution containing 30 μmol L^{-1} of HQ, CC and RC in 10 mmol L^{-1} PBS buffer at pH 7.4 for TCpSi and GCE. In the case of GCE only RC can be correctly determined since the oxidation peaks obtained for HQ and CC totally overlap, whereas in the case of TCpSi

three separate oxidation peaks corresponding to HQ, CC and RC were obtained, allowing the simultaneous determination of the three isomers.

3.3. Analytical performance of TCpSi

The analytical performance of TCpSi for the voltammetric determination of HQ, CC and RC was evaluated. First of all, some experimental parameters such as pH and the stirring time applied to accumulate the compounds on the electrodic surface, were optimized. The voltammetric signals are highly influenced by pH due to the two protons involved in the oxidation processes, which result in a considerable shift to more negative potentials at higher pH values (**Figure S1**). However, from pH 4 to 8 the discrimination between the oxidation peaks of HQ and CC could not be improved because the peaks are shifted with pH at an almost identical rate for the two isomers (**Figure S1d**). In terms of current, the signal increased from pH 4 to 7.5 and slightly decreased at pH 8. Thus, the physiological pH (7.4) was selected as the optimal pH value.

Regarding the stirring time, voltammetric measurements using TCpSi were performed using a solution containing 30 µmol L^{-1} of HQ, CC or RC in 10 mmol L^{-1} PBS buffer at pH 7.4, and varying the stirring time from 0 to 240 s. For all three isomers, the current slightly increased after 30 s of stirring but no further increase was observed for longer stirring times. Therefore, a stirring time of 30 s was selected as the optimal value.

Once the experimental conditions were optimized, the analytical performance of the use of TCpSi for the determination of HQ, CC and RC was studied considering repeatability, reproducibility, sensitivity, linear range and limits of detection (LOD) and quantification (LOQ). All these values are summarized in **Table 2**.

Repeatability was calculated from five consecutive measurements of a solution containing 30 µmol L^{-1} of HQ, CC and RC in 10 mmol L^{-1} PBS buffer at pH 7.4 using the same electrode, whereas reproducibility was computed from the slope of two independent

and individual calibration curves carried out from 0.5 to 50 µmol L^{-1} and using different sensors. For all three isomers, repeatability and reproducibility values lower than 6.5% were achieved. These values are similar to those reported in the literature for GCE modified with different carbon nanomaterials like graphene [18,19], mesoporous carbon [23] or carbon nanotubes [11,20,21], for which repeatability and reproducibility values were in the range of 0.85 – 3.4 % and 4.1 – 6.6 %, respectively. TCpSi's improved reproducibility, added to its advantage of acting as both support and modifier simultaneously, offsets the slightly higher repeatability values obtained. Indeed, the possibility to work with unmodified TCpSi fast-tracks its fabrication process, underpinning mass-production of working electrodes which are stable for long-term storage at room temperature.

In terms of sensitivity, calculated as the slope of the calibration curve, HQ and CC showed similar values, which are significantly higher than that achieved for RC. This agrees with the more intense peaks observed for HQ and CC. On the other hand, LODs and LOQs were calculated as three and ten times, respectively, the standard deviation of the intercept over the slope of the calibration curves. In all cases LOQs were at the level of few µmol L^{-1}, achieving the lowest value for HQ and the highest for RC. However, it should also be pointed out that only RC shows a linear response up to 50 µmol L^{-1}. For HQ and CC, the response was linear up to 35.2 and 25.4 µmol L^{-1}, respectively, leading to linear ranges comparable to those reported by a GCE modified with mesoporous carbon CMK-3 [23] or a commercial graphene screen-printed electrode [16], but narrower than most carbon nanotube-modified GCEs [20, 21, 24]. Although the LODs and LOQs achieved are ~~only~~ slightly higher than those reported in the literature for GCE modified with different nanomaterials [11,18,20,21,23], they are ~~and~~ similar to those reported for a commercial graphene screen-printed electrode [16] (**Table S1**) and below the HQ, CC and RC levels

found in industrial effluents and wastewater, with the additional advantages provided by pSi (versatility, biocompatibility, fast and simple fabrication process, adjustable morphology…). Therefore, the fast electron transfer kinetics and the good analytical performance of TCpSi highlight its potential to act as a new substrate for voltammetric sensors able to discriminate among chemical compounds with similar electroactive behavior.

3.4. Application to the analysis of real samples

The applicability of TCpSi for the voltammetric determination of dihydroxybenzene isomers in real samples was evaluated through the determination of a tap water sample spiked with HQ and CC, as the two most problematic isomers. The simultaneous determination of these two compounds was carried out in triplicate and by means of the standard addition method, considering four successive additions. Representative differential pulse voltammograms for the analysis of the spiked tap water sample using TCpSi as working electrode are shown in **Figure 8**. Well-defined and discriminated peaks that increase linearly with the concentration were obtained for both HQ and CC.

The results obtained from the three replicates of the standard addition calibration are summarized in **Table 3**. Good agreement between replicates, as well as with the expected concentration were achieved for both HQ and CC, resulting in high recoveries and low RSDs, and confirming the applicability of TCpSi to the simultaneous determination of HQ and CC in real samples.

4. CONCLUSIONS

The application of carbon-stabilized pSi, without any additional modifier, as voltammetric sensor platform for the simultaneous detection of three dihydroxybenzene isomers has been successfully demonstrated. First of all, the electrochemical performance of TCpSi and THCpSi with special focus on the repeatability and reproducibility was compared. Second, the electrochemical response of both TCpSi and THCpSi to HQ, CC and RC, was assessed, concluding that TCpSi offers a more reproducible response with faster electron transfer kinetics that results in higher redox reversibility. Interestingly, TCpSi presented a better electrochemical response to HQ, CC and RC than GCE, not only inferred by the higher reversibility, but also by the possibility to simultaneously determine the three dihydroxybenzene isomers. Excellent analytical performance was achieved by TCpSi for the detection of the three isomers, with repeatability, reproducibility and LODs similar to those reported for nanomaterial-modified GCE or screen-printed electrodes. Furthermore, the applicability of TCpSi in real samples was successfully verified through the analysis of a tap water sample spiked with both HQ and CC, achieving high recoveries and precision. Additionally, it should be highlighted that TCpSi retains the unique advantages provided by pSi, such as versatility, biocompatibility, fast and simple fabrication process, and adjustable morphology, which can be harnessed to develop sensing tools fit-for-purpose.

ACKNOWLEDGMENTS

Authors acknowledge financial support from the Australian Research Council's Discovery and Linkage Project Schemes (DP160104362 and LP160101050). Clara Pérez-Ràfols acknowledges the Spanish Ministry of Education, Culture and Sports for a Ph.D (reference FPU15/02140) and mobility (EST17/00326) grant. This work was performed

in part at the Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF).

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Table 1. Peak current and peak potential difference ΔEp (mV) extracted from CV using THCpSi and TCpSi as working electrodes (n=3).

	I_{ox} (µA)	I_{red} (µA)	ΔEp (mV)
THCpSi	328 ± 6	308 ± 12	90 ± 15
TCpSi	364 ± 3	351 ± 6	80 ± 5

*All these values were extracted from the nineteenth CV scan.

Table 2. Calibration parameters, reproducibility and repeatability for the separate determination of HQ, CC and RC prepared in 10 mmol L^{-1} PBS at pH 7.4, after 30 s of stirring, obtained using TCpSi as working electrode. Standard deviations are denoted by parenthesis (n=2).

	HQ	**CC**	**RC**
Sensitivity (µA µmol^{-1} L)	1.41 (0.03)	1.55 (0.08)	0.32 (0.01)
R^2	0.992	0.997	0.990
Linear range (µmol L^{-1})[1]	4.6 – 35.2	8.0 – 25.4	10.4 – 50.0
LOD (µmol L^{-1})	1.4	2.4	3.1
Reproducibility (%, n=2)	2.4	6.2	2.9
Repeatability (%, n=5)	5.1	3.5	5.8

[1] The lowest value of the linear range was considered from the LOQ.

Table 3. Calibration data for the simultaneous determination of HQ and CC, spiked in a tap water sample, by DPV and using TCpSi as working electrode.

	HQ	**CC**
$C_{expected}$ (µmol L^{-1})	5.84	5.84
C_{found} (µmol L^{-1})	5.91	5.76
Recovery (%)	101.4	98.6
RSD (%, n=3)	5.7	5.8

Figure captions

Figure 1. (**a**) Top and (**b**) cross-sectional SEM images of TCpSi nanostructures. The pSi layer was electrochemically etched in a 1:1 (v:v) HF/ethanol solution by applying a current density of 53 mA cm^{-2} for 20 s in a MPSB wet etching system.

Figure 2. (**a**) FTIR and (**b**) Raman spectra of freshly etched pSi, THCpSi and TCpSi. The pSi layer was electrochemically etched in a 1:1 (v:v) HF/ethanol solution by applying a current density of 53 mA cm^{-2} for 60 s in a MPSB wet etching system.

Figure 3. Stability test of pSi, THCpSi and TCpSi incubated in aqueous PBS buffer (pH 7.4) based on reflective interferometric Fourier transform spectroscopy measurements. (**a**) Typical Fourier transform of the reflectance spectrum (inset) of a pSi single layer with a pore diameter of 12 ± 5 nm and a thickness of 1.6 µm. (**b**) Plot of the ΔEOT% measured in air against incubation time in PBS.

Figure 4. (**a**) 20 consecutive CV scans measured in a 2 mmol L^{-1} ferrocyanide/ ferricyanide solution in 10 mmol L^{-1} PBS buffer at pH 7.4 using THCpSi and TCpSi; (**b**) nineteenth CV scans corresponding to replicates of three THCpSi and three TCpSi samples.

Figure 5. Cyclic voltammograms obtained when testing a 30 µmol L^{-1} (**a**) HQ, (**b**) CC or (**c**) RC solution in 10 mmol L^{-1} PBS buffer at pH 7.4, using GCE (blue line), TCpSi (red line) and THCpSi (green line). GCE currents are referred to the right axis whereas TCpSi and THCpSi currents are referred to the left axis.

Figure 6. Redox reactions of (**1**) HQ, (**2**) CC and (**3**) RC.

Figure 7. Differential pulse voltammograms obtained for a solution combining 30 µmol L^{-1} HQ, CC and RC in 10 mmol L^{-1} PBS at pH 7.4, using TCpSi (red lines) and GCE (blue lines) as working electrode. GCE currents are referred to the right axis, whereas TCpSi currents are referred to the left axis.

Figure 8. Differential pulse voltammograms obtained for the simultaneous determination of HQ and CC, spiked in a tap water sample, using TCpSi as working electrode at pH 7.4 following the above stated electrochemical conditions. Inset: standard addition plots.

Figure 1

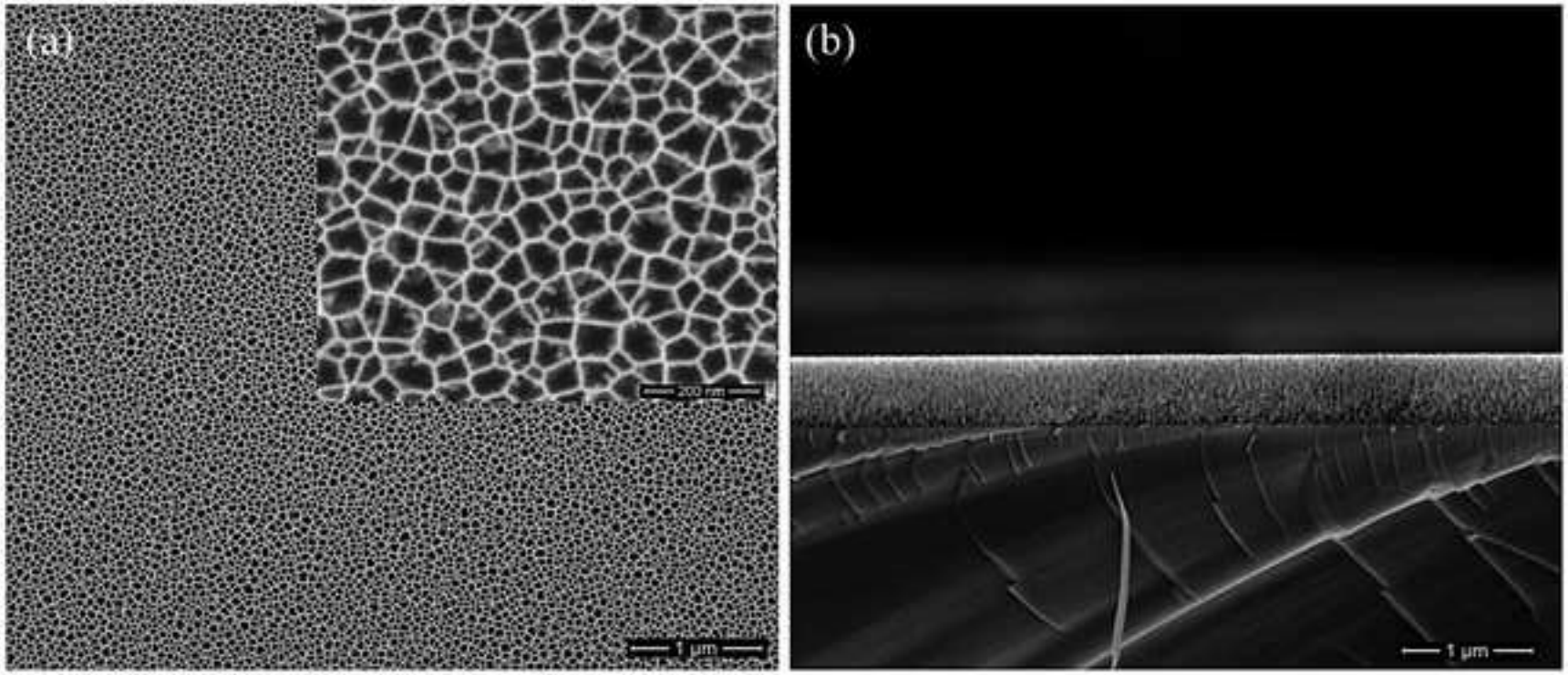

Figure 2

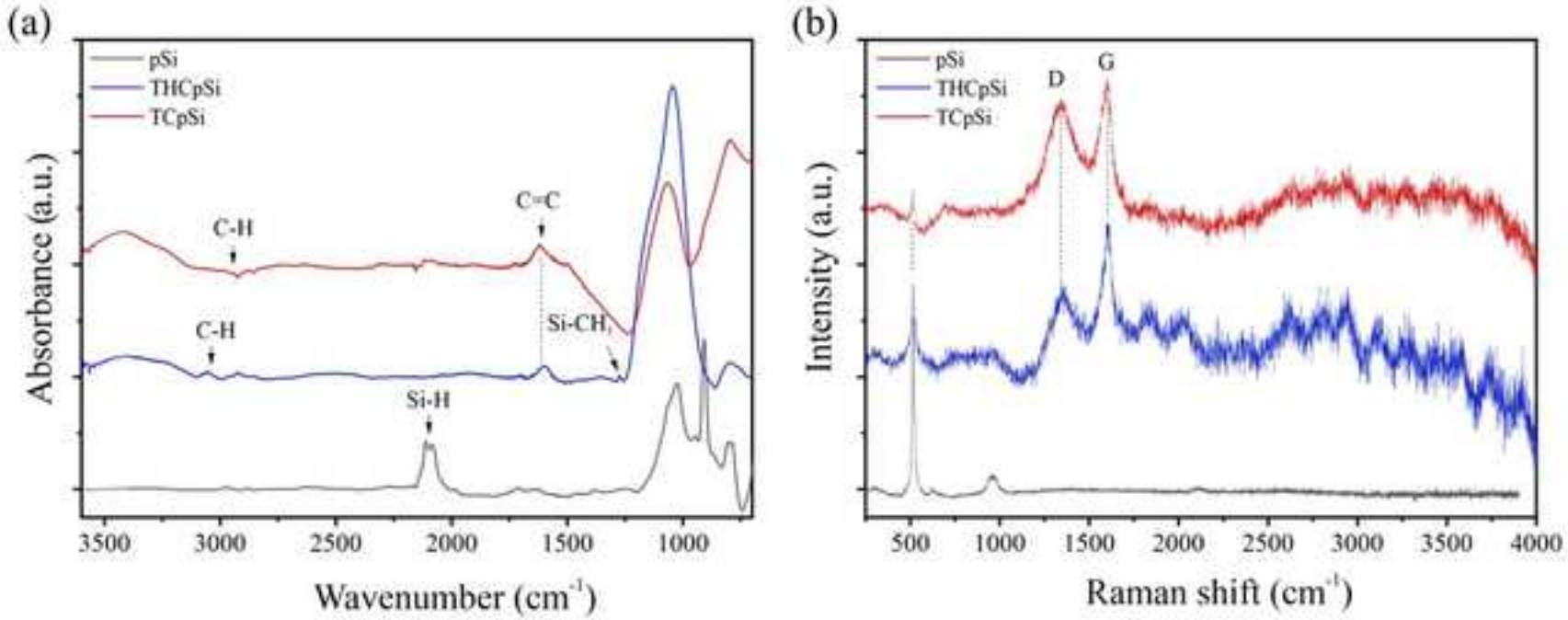

Figure 3

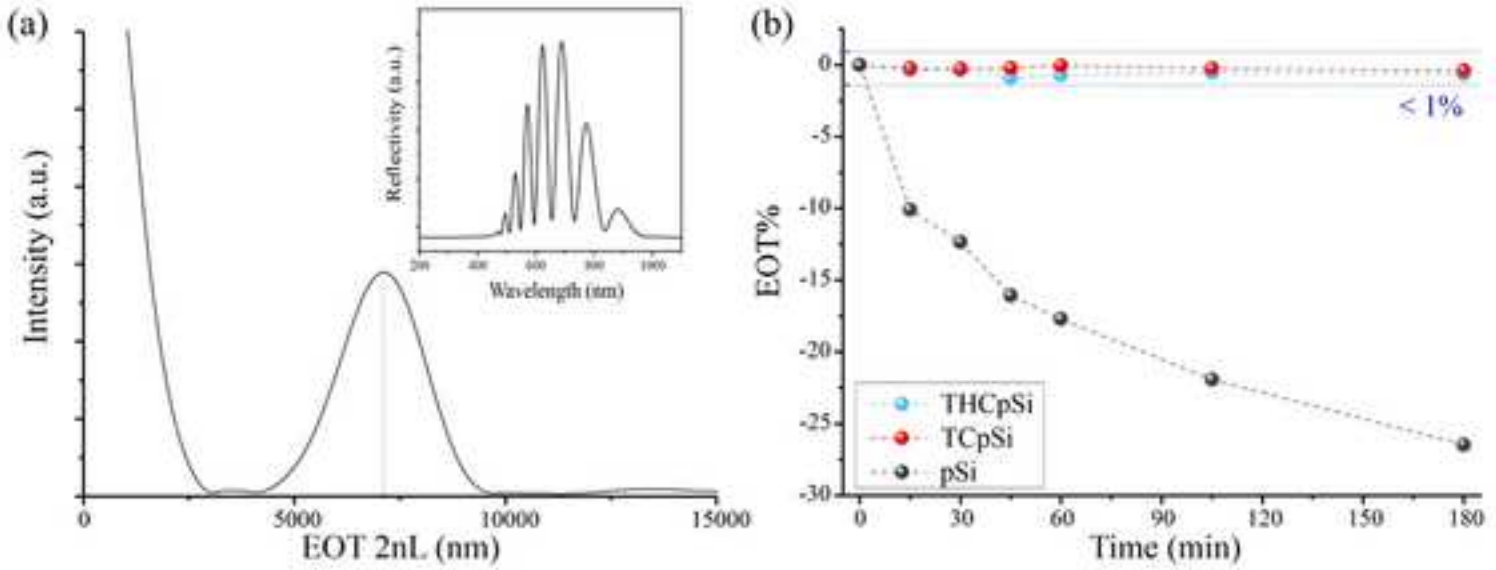

Figure 4

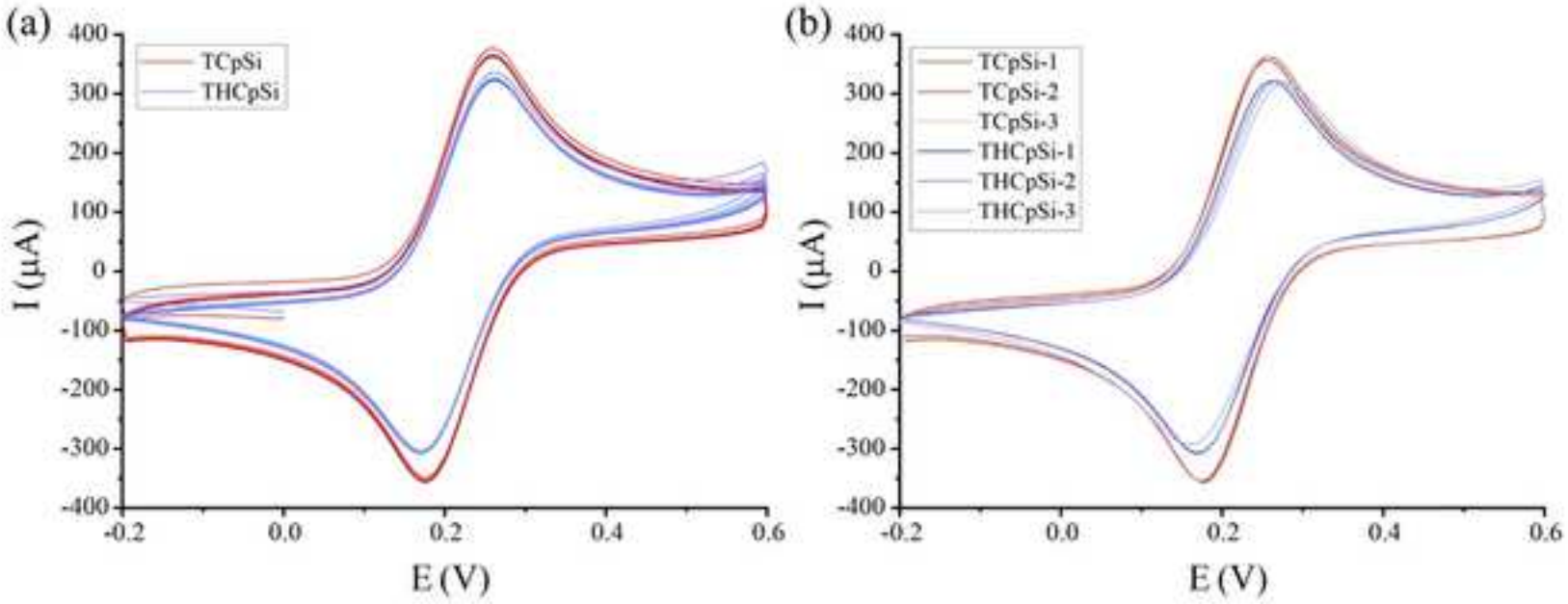

Figure 5

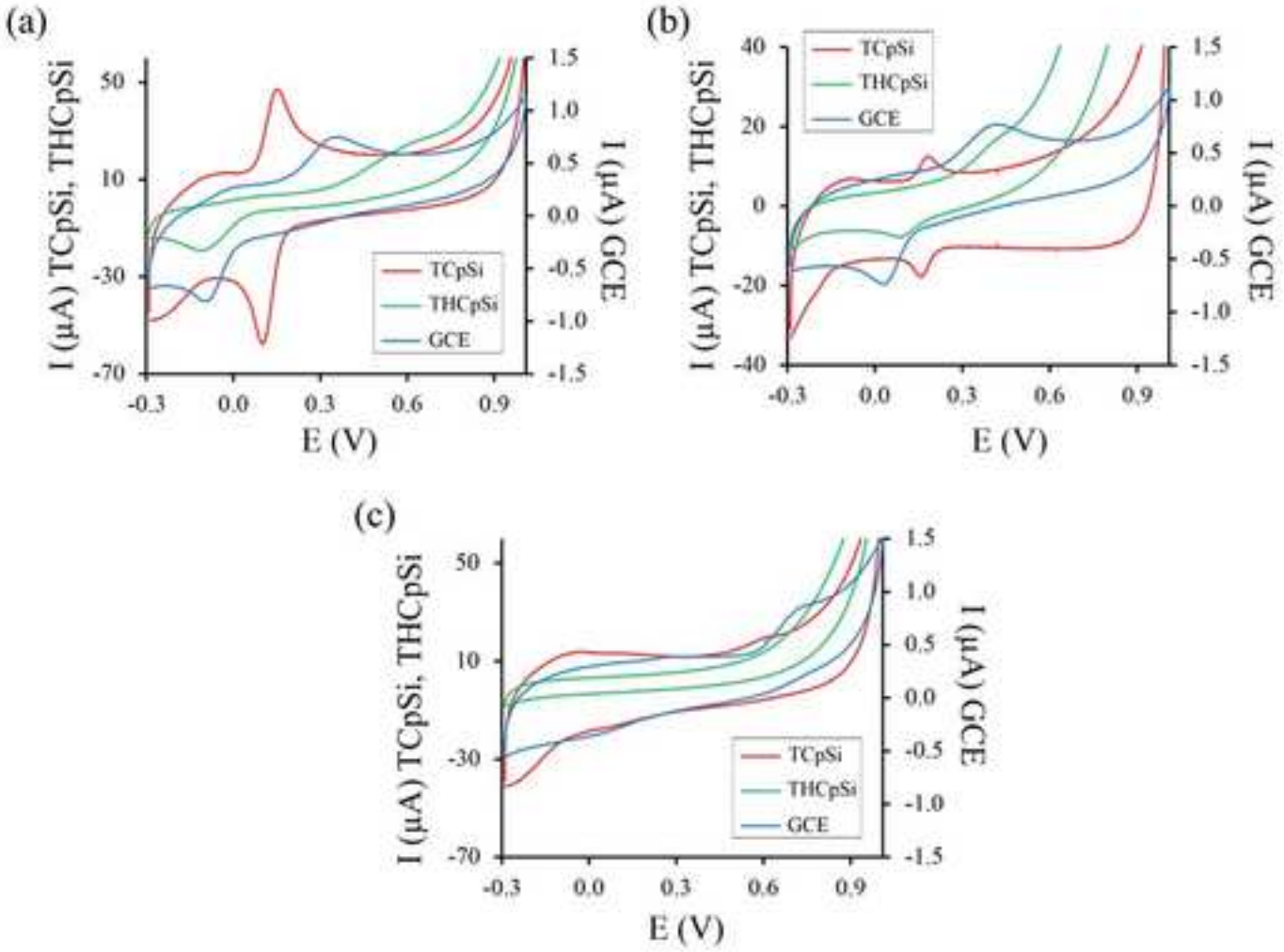

Figure 6

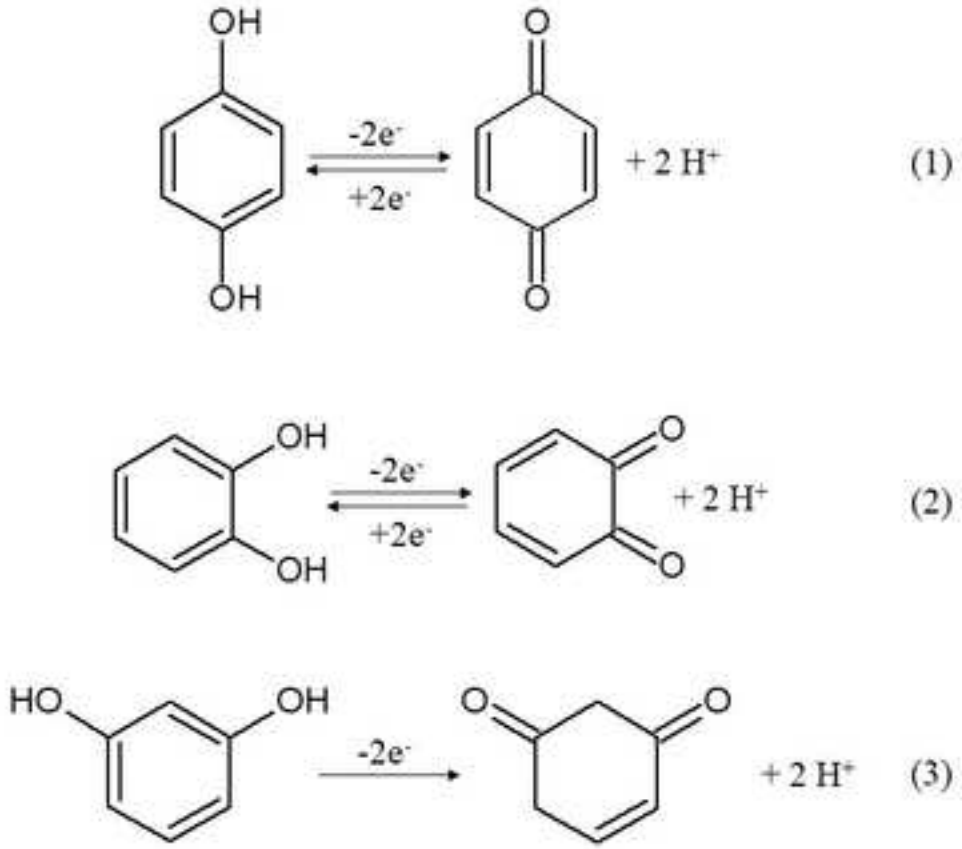

Figure 7

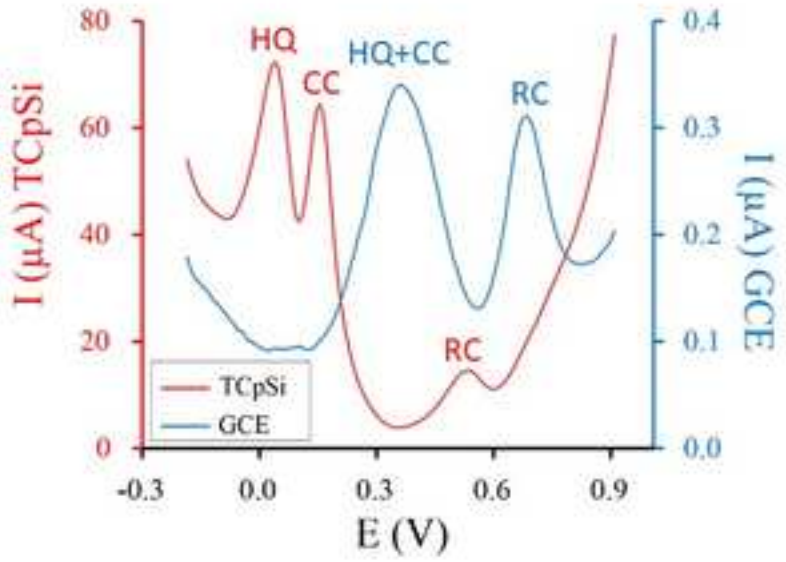

Figure 8