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Activation of commercial Pt/C catalyst towards glucose electro-oxidation by irreversible Bi adsorption

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Abstract

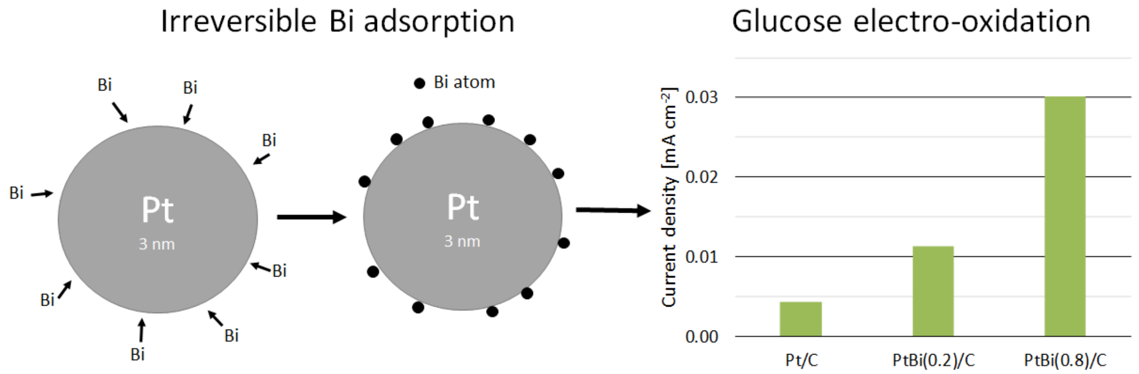
The effect of irreversible adsorbed Bi on commercial Pt/C catalyst towards glucose electro-oxidation reaction (GOR) in different electrolytes (acidic, neutral, alkaline) is studied. Bi is successfully deposited on Pt/C from Bi^{3+} containing acidic solution from 0 to 90% coverage degree. The stability of the Bi layer in acid and alkaline corresponds to previous studies and starts dissolve at 0.7 V and 0.8 V vs reversible hydrogen electrode (RHE), respectively. However, in neutral phosphate buffer the layer shows remarkable stability to at least 1.2 V vs RHE.

Bi modification at low (20%) and high (80%) coverage show the highest increase in the activity of Pt/C towards GOR by a factor up to 7 due to increased poisoning resistance of the modified catalyst. The effect of poisoning is especially reduced at high Bi coverage (80%), which shows that adsorbate blocking by Bi through the third-body effect is effective. Finally, with or without Bi modification GOR on Pt/C is most active in alkaline conditions.

Keywords

Glucose electro-oxidation; Platinum; Bismuth; Catalyst poisoning; Renewable resources

Graphical abstract



Glucose electro-oxidation rate on carbon supported Pt nanoparticles can be increased up to 600% by irreversibly adsorbing Bi on Pt. This also improves the poisoning resistance of Pt towards glucose and its oxidation products.

1 Introduction

Glucose is an important biomolecule that is ubiquitous in nature. In electrochemistry, it is studied in two main applications: as a detectable species for sensors [1] and as an energy source [2,3]. In the former case, especially the increasing blood glucose levels related to diabetes require fast and reliable detection methods. In the latter case, implantable fuel cells deriving their energy from glucose and oxygen in the blood stream have attracted attention. In addition, with effective catalysis energy conversion from glucose-containing waste streams directly to electricity could be realized instead of bacterial hydrogen production [4].

The catalysis of the glucose electro-oxidation reaction (GOR) can be divided into two groups based on the catalyst material. In enzymatic glucose electro-oxidation, enzymes found in nature, like glucose oxidase, are used as catalysts [5]. They are highly sensitive and selective but suffer from poor stability and require a very specific environment to work [2]. Therefore, non-enzymatic glucose electro-oxidation based on more robust metallic catalysts has been studied widely.

Among different metals, Pt has been shown to be active towards GOR, especially in alkaline conditions [3]. Glucose itself is adsorbed in the hydrogen adsorption region and loses one electron [6]. This adsorbed species can then react further to an adsorbed gluconate species in the double-layer region or to an adsorbed d-gluconolactone. These products slowly desorb from Pt limiting the performance of the catalyst. The oxidation also proceeds only to gluconate releasing 2 electrons per glucose molecule instead of maximum 24 electrons available through total oxidation to CO_2. Although further oxidation is possible, it is much slower than GOR [7,8]. Furthermore, the activity of Pt is lower in acidic and neutral conditions, which are important for fuel cell and biological applications, respectively. This problem has been approached with the decoration of Pt by heavy metal atoms, like Bi, Pb and Sb, which can enhance the kinetics of GOR on Pt [9-17]. The proposed explanations for the enhancement are bifunctional mechanism, where the less noble metal provides oxygen-containing species for the oxidation at lower potentials than Pt, third-body effect, where the adatom blocks or weakens the adsorption of poisoning intermediates or a complex formed by Bi and glucose [12].

The previous studies of GOR at Pt with adatoms have commonly placed the adatom at low concentrations in the electrolyte [9-14], so they adsorb and desorb from the surface according to potential. This does not allow for a constant adatom coverage over the entire potential range and the presence of the adatom in the electrolyte complicates or prohibits practical applications of the modified catalyst. However, irreversible adatom adsorption on Pt surfaces has been used extensively for example with formic acid [18,19], ethanol [20] and glycerol [21] electro-oxidation. In this method, the adatom is simply introduced on Pt by dipping the electrode in a solution containing the wanted metal ions at open-circuit potential eliminating the need for their presence in the studied glucose solution. Scanning tunneling microscopy (STM) studies have shown multilayer islands of Bi formed on the Pt surface, which are reorganized to monolayer islands through reduction and oxidation of Bi [22,23]. Bi atoms are highly mobile on the Pt surface and form ordered structures when the surface is exposed to other adsorbates [24], which has been seen with STM [25], low energy electron diffraction [26] and X-ray scattering studies [27].

There are only few studies employing this method for GOR published previously [15-17,28]. Miao et al. [17] used a Pt disc electrode for Bi adsorption and showed increased activity in NaOH compared to a clean Pt disc. On the other hand, Bi did not have significant influence on the activity in sulfuric acid. The effect of the electrode exposure time and the concentration of the Bi solution for GOR activity in alkaline was studied but the actual Bi coverage on Pt was not analyzed. Maximum performance was achieved after 15 minutes in contact with a solution of 0.4 mM Bi^{3+}. In a follow-up study, they used self-synthesized Pt nanoparticles on a glassy-carbon electrode with similar results [28]. Daniele et al. [16] fabricated mesoporous Pt and coated it irreversibly with Bi under potential control. This resulted in greatly enhanced GOR activity at Bi coverage 0.9 compared to the uncoated Pt electrode in 0.2 M NaOH. Hazzazi et al. [15] used single-crystal electrodes (Pt{321}) and irreversibly adsorbed Bi, Ag and Au on them. Of these only irreversibly adsorbed Bi increased GOR activity in 0.1 M H_2SO_4 and the improvement was optimal at low coverage (<0.5).

These previous studies have presented many positive results with adatom modified Pt for GOR. However, from application point of view, they are usually made with Pt disc electrodes and not with the nanostructured, high specific surface area Pt that is used in modern electrocatalytic applications with the exception of Yang et al. [28], where self-synthesized Pt nanoparticles on glassy-carbon electrode were used. In addition, different pH values are preferred in the different applications: acidic fuel cells work best, *in-situ* biological application require neutral environment and GOR kinetics are fastest in alkaline. This requires the testing of a potential catalyst for GOR in all these electrolytes and this has not been made with irreversibly adsorbed adatoms on Pt. Furthermore, it is necessary for energy applications that the catalyst works for extended periods under flow conditions (*e.g.* fuel cells, blood stream) requiring chronoamperometric studies on catalyst activity over time.

In order to investigate these factors, commercial supported Pt nanoparticles on activated carbon catalyst (Pt/C) from Alfa Aesar is used in this study. Bi was selected as the adatom because of its promising activating effect in previous studies and its environmentally benign nature. The effect of Bi coverage on GOR in an acid, neutral and alkaline electrolyte is examined with cyclic voltammetry and chronoamperometry. The stability of the Bi in the different electrolytes is also studied in order to understand the potential limitations in different environments and applications.

2 Material and methods

All the chemicals were purchased from Sigma-Aldrich except for Pt (60 wt%) on activated carbon and alkaline FAA3 ionomer solution, which were obtained from Alfa Aesar and Fumatech, respectively.

Electrodes for the GOR characterization were made from a catalytic ink. For acidic and neutral electrolyte testing, 5 mg of Pt/C was mixed with 100 µL 1-propanol and 100 µL deionized water as solvents with a magnetic stirrer for 5 min and 10 µL of 5 wt% Nafion solution was added. The ink was further mixed with a magnetic stirrer for several hours and sonicated for 15 min in between. A 4 µL aliquot was placed on a polished glassy-carbon disc electrode (Æ5 mm, GCE) and it was let to dry overnight in ambient conditions. In the alkaline case, N-methylpyrrolidinone was used as the solvent and 5 µL of 12 wt% FAA3 solution was added instead of Nafion to ensure alkaline environment for the catalyst. 2µL aliquot was deposited twice on the electrode with drying a vacuum oven in between (40 °C, 10 min).

The electrochemical measurements were made with two separate cells. The first cell contained 0.1 M $HClO_4$ electrolyte and the second in either 0.1 M $HClO_4$, 0.05 M phosphate buffer at pH 7 (PBS) or 0.1 M NaOH with or without 0.1 M D-glucose. In both cells, the prepared GCE electrode was the working electrode, a Pt wire the counter electrode and a reversible hydrogen electrode (RHE) the reference electrode. All the potentials in this paper are presented against the RHE. Autolab PGSTAT100 was used to control the potential and current of the cell. The control software was GPES and smoothing was done to cyclic voltammograms (CV) to remove small periodical noise from the data. All the electrochemical measurements were made after purging the cell from O_2 by N_2 bubbling for 20 minutes.

The Pt/C electrode was first cleaned with CO adsorption/stripping procedure, where CO was bubbled through the cell for 5 minutes, changed to N_2 for 10 minutes and finally CO was oxidized by 3 consecutive CVs from 0.05 to 1.2 V. The active Pt surface area was then calculated from the H adsorption/desorption peaks by scanning the potential between 0.05 and 0.6 V until stable CV was achieved. The currents in this paper are normalized against this area. The charge involved was determined by subtracting the lowest current value in the double-layer region from the H desorption current and then integrating the difference between 0.05 and 0.45 V.

Bi was irreversibly adsorbed on the Pt/C electrode by dipping at open circuit potential. 2 mM Bi^{3+} solution in 0.1 M $HClO_4$ was prepared from $Bi(NO_3)_3 \cdot 5\ H_2O$. The cleaned electrode was dipped in the solution for a period of time and rinsed thoroughly. After it was transferred back to the cell containing 0.1 M $HClO_4$, the H adsorption/desorption area was again determined. Considering H does not adsorb on Bi [29], the coverage of Bi could be estimated from the decrease in H desorption charge using equation

$$\theta_{Bi} = \frac{Q_{H,Pt}-Q_{H,PtBi}}{Q_{H,Pt}}, \tag{1}$$

where $Q_{H,Pt}$ is the H desorption charge on clean Pt/C and $Q_{H,PtBi}$ the H desorption charge after Bi has been adsorbed on the Pt surface. Bi coverage in this article is presented as PtBi(q_{Bi}). To achieve high coverage PtBi(>0.6), $Bi(NO_3)_3 \cdot 5\ H_2O$ was added to the dipping solution so that the Bi^{3+} concentration was approximately 20 mM. If the achieved coverage was less than desired, dipping was repeated. If the coverage was higher than desired, the electrode was kept at 1.2 V with rotation to etch Bi from Pt surface. These procedures were repeated until satisfactory coverage was realized (±0.03 from the target value). To ensure that the dissolved Bi did not interfere with the measurements, a CV was recorded in 0.1 M $HClO_4$, where Bi coverage had been etched from 0.87

to 0.35 (corresponds to 11 minutes at 1.2 V), and compared with a CV measured with the same electrode in a fresh electrolyte (Fig. S1). The CVs were practically identical proving that the small amount of Bi etched from the electrode does not affect the measurements.

The stability of the adsorbed Bi was measured by transferring the electrode to a cell containing the studied electrolyte for etching. In the case of 0.1 M $HClO_4$, the same cell was used for the coverage determination and etching. Approximately PtBi(0.55) was deposited on Pt/C for the testing. Potential of the electrode was kept at a constant potential for 10 minutes under 300 rpm rotation and the coverage was measured again after this. The potential was increased step-wise with 0.1 V intervals up to 1.1-1.2 V to determine when the Bi layer started to dissolve.

GOR activity of Pt/C and PtBi/C electrodes were measured by transferring the electrode to the cell containing 0.1 M glucose and the studied electrolyte. Cyclic voltammetry was performed at Pt, PtBi(0.2), PtBi(0.4), PtBi(0.6) PtBi(0.8) and PtBi(0.9) to study the effect of Bi coverage on the GOR activity of the catalyst. CVs were measured from 0.05 to 0.8 V according to the stability measurements. For further analysis, the most promising coverages PtBi(0.2) and PtBi(0.8) were selected for chronoamperometric measurements at 0.4 and 0.6 V with 100 rpm rotation and compared with clean Pt. The electrode was cleaned by a 2-second potential excursion to 1.2 V before applying the measured potential. According to a separate dissolution test, this results in maximum dissolution 2% of Bi so its effect to coverage is not significant. For any measurement series, the same electrode was used for the different Bi coverages starting from the lowest coverage and Bi added after cleaning the electrode from glucose and its oxidation species by potential cycling in 0.1 M $HClO_4$ from 0.05 to 1.2 V for 10 cycles so that the CV was stable.

3 Results and discussion

3.1 Stability of irreversibly adsorbed Bi on Pt/C

The CVs of the Pt/C electrodes with different Bi coverages determined from Eq. 1 in 0.1 M $HClO_4$ are presented in Fig. 1.

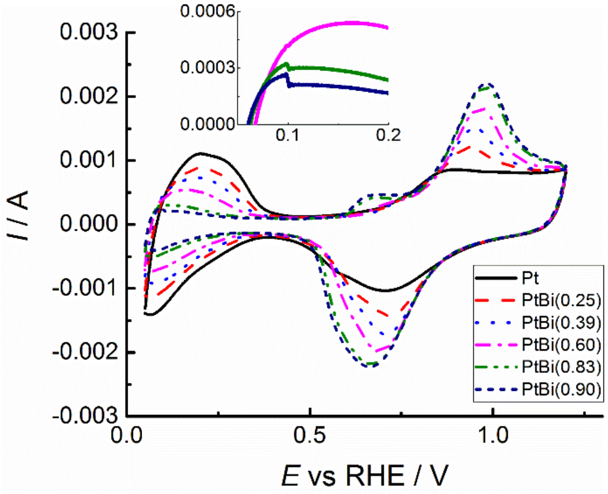


Figure 1. Cyclic voltammograms measured in 0.1 M $HClO_4$ with different Bi coverages on the electrode (0.02 V s^{-1}). The inset shows the potential region around 0.1 V vs RHE for high Bi coverage between 0.6 and 0.9.

It can be seen from Fig. 1 that as expected the H adsorption region between 0.05 and 0.45 V is suppressed as the Bi coverage increases due to longer dipping times in Bi^{3+} solution. On the other hand, a new peak pair appears at around 0.95-1.00 V on the positive sweep and at 0.65-0.70 V on the negative sweep. This redox peak pair has been attributed to Bi before [30,31] and its intensity increases with Bi coverage. When the coverage reaches high values of over 0.60, another positive peak appears at 0.65 V. This may be due to Bi adsorption on different crystal surfaces of the polycrystalline/-oriented Pt nanoparticles as Bi on Pt(111) has been shown to react at lower potentials (0.61 V vs RHE) than on Pt(100) or Pt(110) (> 0.8 V vs RHE) [30]. This would indicate that Bi is preferentially adsorbed on these surfaces, instead of Pt(111), on the carbon supported Pt nanoparticles.

In the inset of Fig. 1 at the starting and ending point of the CV (0.1 V), a jump to a higher current can be observed after a potential excursion to 1.2 V for high Bi coverage. This suggests that more Pt sites are exposed and available for H adsorption/desorption. One explanation is that Bi has been desorbed from or rearranged on Pt during the CV. The exact mechanism is not clear but the result indicates that the Bi may not be stable at all potentials. Consequently, the stability of the Bi layer as a function of potential was studied in acidic, neutral and alkaline environments to ensure that Bi layer remains stable during GOR.

In Fig. 2, the coverages of single electrodes are presented after potential holds of 10 min in the different electrolytes at increasing potential values. The starting coverage was approximately 0.55 for each case. It is immediately clear that the pH affects Bi stability significantly. In 0.1 M $HClO_4$, the Bi layer starts to dissolve at 0.8 V, which is in agreement with previous results in 0.5 M H_2SO_4 [32]. In neutral 0.05 M PBS buffer, there is no change in the coverage up to at least 1.2 V indicating a very stable Bi layer. In 0.1 M NaOH, the coverage starts to decrease at 0.9 V but not as strongly as in $HClO_4$. In this case, there is also a decrease of coverage from 0.54 to 0.47 during the first potential hold. This sudden decrease, which was not observed in acid or neutral conditions, can be a results of a Bi layer reorganization into larger islands in an alkaline solution [24,31].

The differences in stability in the various electrolytes may be explained by the oxidation potential of Bi. It has been previously shown that the Bi oxidation peak is at higher potential in an alkaline than in an acidic electrolyte (0.66 and 0.63 V vs RHE, respectively) [31] and that Bi nanoflower structures on Pt in neutral PBS only oxidize at approximately 0.9 V vs RHE [33]. It is therefore likely that the oxidized Bi species are more prone to dissolve from the electrode than reduced Bi.

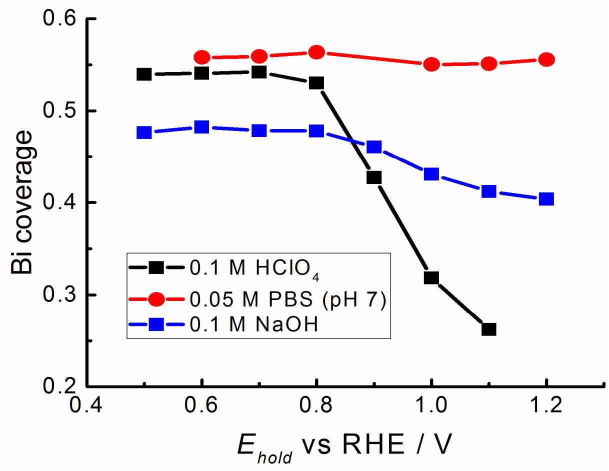


Figure 2. The Bi coverage of PtBi/C electrodes in the acidic, neutral and alkaline electrolytes after holding the potential at values indicated on the x-axis for 10 min.

Bi stability was still further studied in 0.1 M $HClO_4$ with potential cycling at a stationary electrode. Fig. S2 shows the Bi coverage of an Pt/C electrode after cycling the potential between 0.05 and different maximum potentials for 50 times at 0.05 V s^{-1}. The electrode is more stable than during potential hold in the same electrolyte and the coverage does not decrease until 1.0 V is set as the maximum cycle potential. One possible explanation for this could be that desorbed Bi is readsorbed from the vicinity of the electrode during each negative sweep of the potential cycle making the layer appear more stable during quick potential cycling (0.05 V s^{-1}) than a long potential hold (10 min). There is also a slight increase in coverage with lower maximum potentials that could indicate Bi layer reorganization *e.g.* from multilayers to monolayers as the potential of dissolution is approached.

Based on the stability measurement of irreversibly adsorbed Bi layer on the commercial Pt/C catalyst, the glucose oxidation measurements were decided to be performed at maximum 0.8 V for

CVs and at 0.6 V for chronoamperometric measurements. Same maximum potentials were used for all the electrolytes for better comparison.

3.2 Glucose electro-oxidation activity of Bi adatom modified Pt/C

CVs of Pt/C and PtBi/C at different coverages in 0.1 M glucose solution and the various electrolytes are presented in Fig. S3a (0.1 M $HClO_4$), S4a (0.05 M PBS) and S5a (0.1 M NaOH). From the different coverages, PtBi(0.2) and PtBi(0.8) were determined to give best results in terms of GOR activity and were selected for further study (Fig. S3b, S4b and S5b). Relative current change in the positive sweep with Bi addition compared to Pt/C (enhancement factor, I_{PtBi} / I_{Pt}) is presented in Fig. 3 and Fig. S3c, S4c and S5c.

From Fig. S5b, it is immediately clear that GOR on the clean Pt/C catalyst is fastest in alkaline conditions with current density exceeding 0.015 mA cm^{-2} at potentials higher than 0.3 V. In $HClO_4$, the current density remains under 0.015 mA cm^{-2} until very high potentials (>0.75 V), and in PBS the electrochemical reaction proceeds even more slowly (0.003-0.008 mA cm^{-2}) at all potentials. However, with Bi modification significant changes in GOR can be achieved in the different electrolytes.

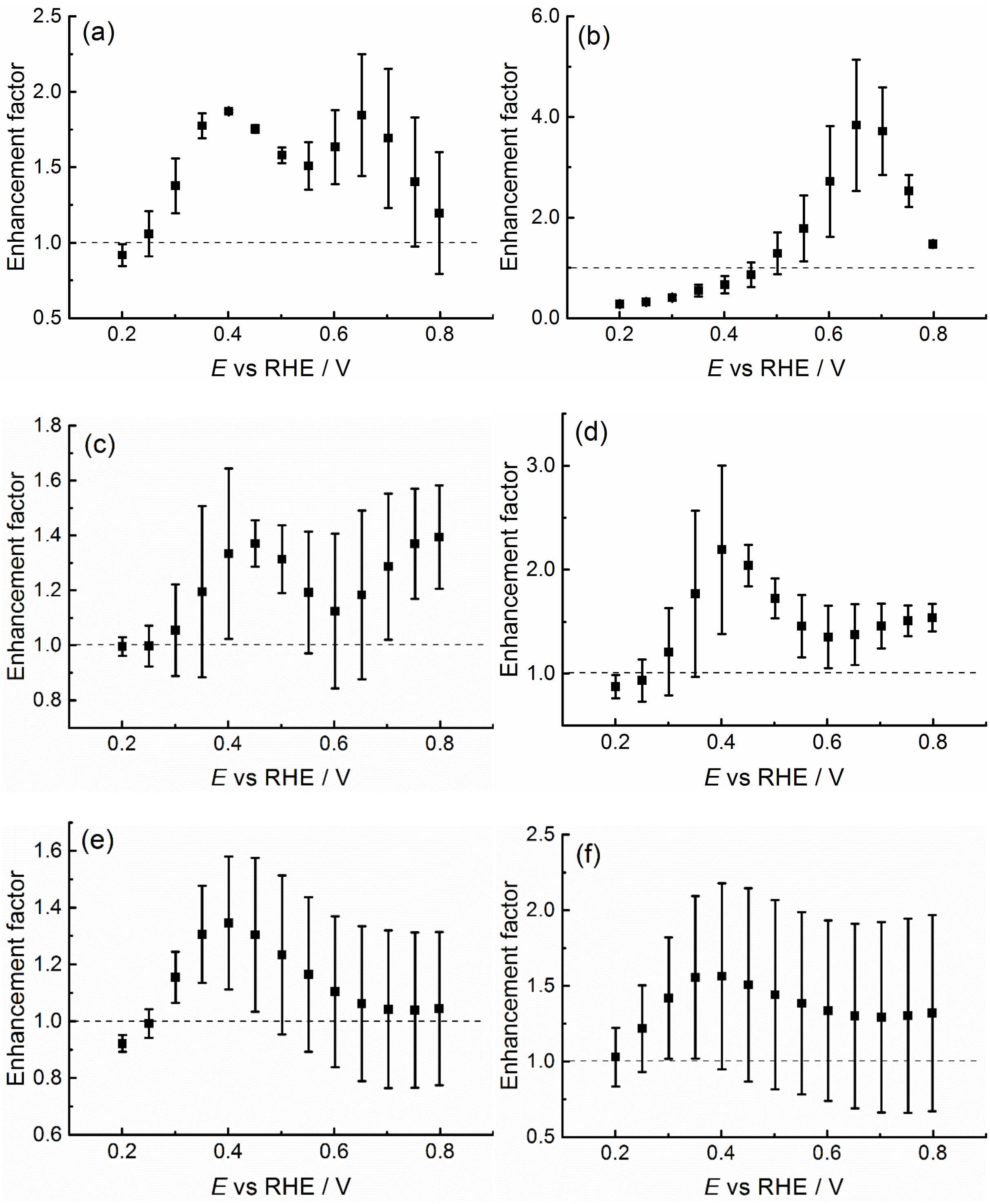


Figure 3. Enhancement of glucose (0.1 M) electro-oxidation current compared to the Pt/C electrode with Bi coverage of 0.2 (a,c,e) and 0.8 (b,d,f) in 0.1 M HClO4 (a,b), 0.05 M phosphate buffer (c,d) and 0.1 M NaOH (e,f). Data taken from the positive sweep of CVs (0.02 V s^{-1}). The dotted line shows enhancement factor value 1, where the performance is the same as with Pt/C.

In the case of 0.1 M $HClO_4$ (Fig. S3b), there are clearly two different mechanisms for the Bi covered electrodes depending on the Bi coverage level. At PtBi(0.2), the oxidation current density compared to Pt/C is increased up to 1.8 times between 0.2 and 0.8 V (Fig. 3a). Similar current densities to Pt/C below 0.2 V suggests that even though the poisoning adsorption of glucose on Pt is not affected by the low Bi coverage, the resulting gluconate and gluconolactone species are more lightly bound to the surface and desorb faster at higher potential [6]. At PtBi(0.8), there is a clear repression of current density at low potentials between 0.05 and 0.4 V compared to Pt/C but on the other hand, a nearly 4-fold increase centering around 0.65 V. This can indicate that adsorption of glucose is inhibited by Bi and that its oxidation starts at high potential but at a high rate due to the absence of adsorbed and dehydrated glucose. These results prove that low GOR activity of a commercial Pt/C catalyst in acidic solution can be improved and tuned by irreversible Bi adsorption at different coverages, which can be applied for example in acidic Nafion-based fuel cell for energy production from glucose containing solutions.

In the case of 0.05 M PBS at pH 7, GOR current densities increase from 0.3 to 0.8 V much like in $HClO_4$ (Fig. S4b). However, the difference between the low and high Bi coverage is not as pronounced. As with $HClO_4$, the highest current density is achieved by PtBi(0.8) but already at 0.4 V (enhancement factor 2.1). At over 0.6 V, the different coverages yield similar results and enhancement is smaller at approximately 1.2 (Fig. 3c-d). The current densities at 0.05-0.2 V are similar to Pt/C, so it appears that in neutral electrolyte glucose is adsorbed on a PtBi surface as on a Pt surface but that its oxidation and the desorption of gluconate and gluconolactone are enhanced by Bi. Finally, improving the activity of Pt towards GOR in a neutral media is important for glucose fuel cells and sensors as implanted devices or working in other glucose containing environments, like waste streams.

In 0.1 M NaOH, Bi modification has not as large effect on glucose electro-oxidation activity of Pt as in acid and neutral electrolytes. There is an improvement only between 0.25 and 0.5 V (enhancement factor up to 1.3) and the behavior is similar with both PtBi(0.2) and PtBi(0.8) (Fig. 3e-f). Otherwise the performance of the electrodes is quite similar or even lower than with Pt. This is likely due to the good activity of the Pt surface in alkaline conditions towards GOR [7,8] and that it cannot be improved as significantly as in acidic and neutral electrolytes. It is however noteworthy that some improvement can be achieved at low potential region, which is promising especially for fuel cell applications as low anode potential results in a high operating potential.

The CV shape of glucose electro-oxidation on Pt/C is different compared to what has been previously published. There are less peaks in studied potential range and they are not as distinct as measured for example with a microspherical Pt electrode [34] or with Pt nanoparticles [28,35]. It is beyond the scope of this paper to ascertain the reason for this but some explanations can be speculated. Firstly, the potential window we used is narrower (to 0.8 V) than in the previous studies as we wanted to avoid Bi dissolution that is not a problem for a pure Pt/C catalyst. Some electrochemical processes for glucose oxidation on Pt happen only at potential higher than 0.8 V [6] and thus can influence the shape of the CV. Furthermore, it has been shown that with larger nanoparticles more peaks are evident during glucose electro-oxidation [36]. As our commercial catalyst contains very small Pt nanoparticles (< 3 nm), it is possible that this influences the low number of CV peaks. Finally, it is well known that the carbon support material affects the electrochemical properties of the Pt nanoparticles [37]. The support was activated carbon in our case while it has been glassy carbon [28] and carbon black (Vulcan) [35] in previous studies on Pt nanoparticles.

From Fig. 3, it can be seen that there are large deviations in the enhancement factors measured in each of the electrolytes. Indeed, the current densities during the CV measurements are quite unstable and vary from one cycle to another even with a single electrode leading to uncertain results. Fig. S6 shows the current density values at different potentials in the positive sweep from one electrode during 3 sets of 10 CVs in 0.1 M $HClO_4$. Noticeable and random fluctuations are obvious and no stable CV is reached. This could be due to glucose and the various products from its electro-oxidation gathering and reacting on the stationary electrode. Therefore, the activity and poisoning resistance was further studied with chronoamperometry under constant electrode rotation to improve the reproducibility of the results and also have the conditions closer to a real environment with convective flows and mixing.

Based on the optimum enhancement of GOR measured with CVs, 0.4 and 0.6 V were selected as potentials for chronoamperometric measurements. The resulting chronoamperometric curves in different electrolytes are presented in Fig. S7. The current density of the PtBi/C electrodes in relation with the current density of the Pt/C electrode at different time points are presented in Fig. 4 (enhancement factor I_{PtBi} / I_{Pt}). In comparison with the CV results, more remarkable increases in performance can be seen in all the electrolytes.

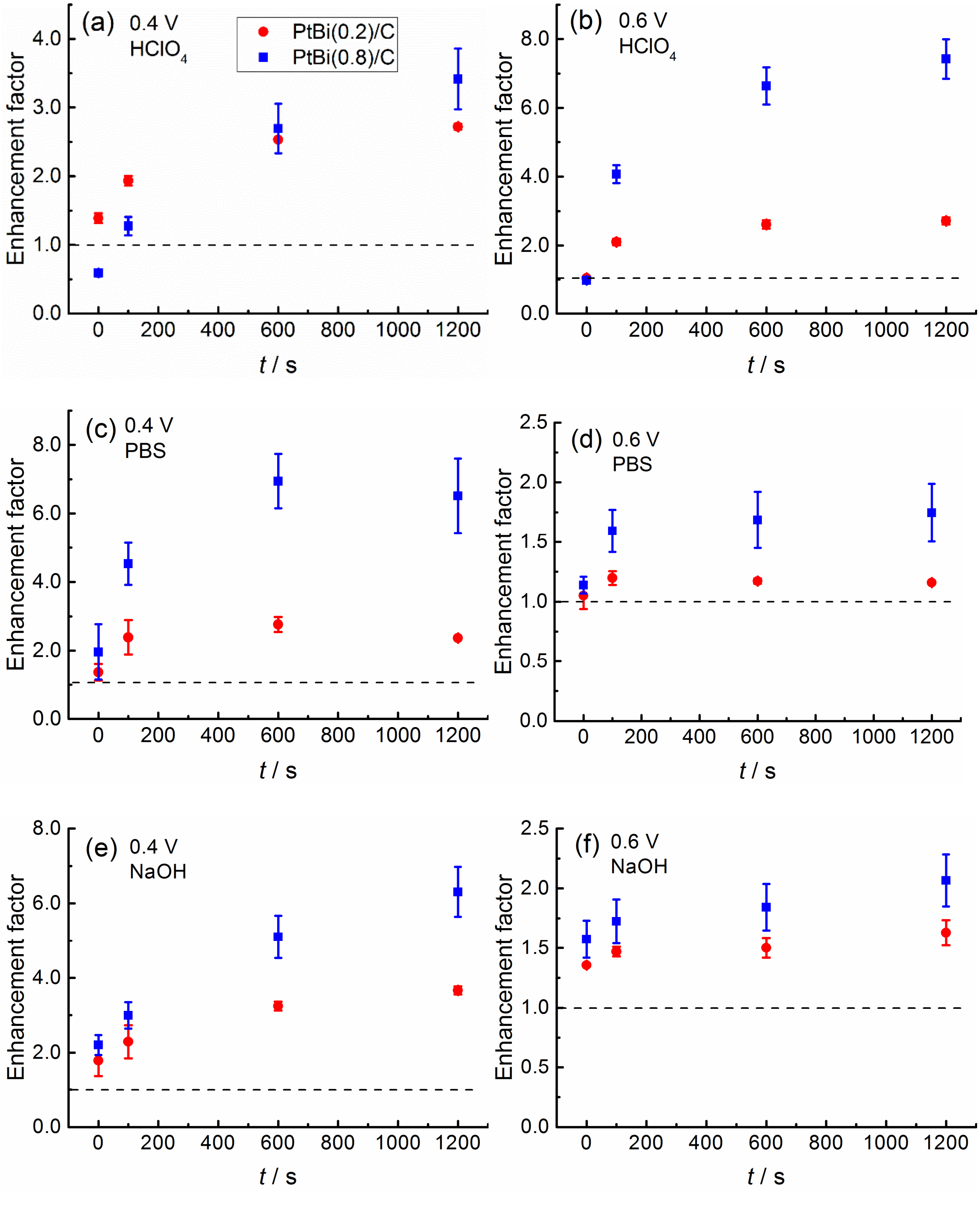


Figure 4. Enhancement of glucose (0.1 M) electro-oxidation current compared to the Pt/C electrode with Bi different coverage in 0.1 M HClO4 (a,b), 0.05 M phosphate buffer (c,d) and 0.1 M NaOH (e,f) at 0.4 V (a,c,e) and 0.6 V vs RHE (b,d,f). Data taken from chronoamperometry (100 rpm) at different time points. The dotted line shows enhancement factor value 1, where the performance is the same as with Pt/C.

In 0.1 M $HClO_4$, the Pt/C electrode does not perform very well (Fig. S7a-b). The current density decreases steeply over the first 200 s and at slower pace during the rest of the experiment approaching zero. This corresponds to the results by Kokoh et al. [7] who reported that the current quickly reaches zero unless a high potential step (1.1 V vs RHE) for the cleaning of the Pt surface is used. Current density is higher at 0.6 V, which is expected as adsorbed glucose can oxidize further [6]. At PtBi(0.2)/C, the curve shape is similar to Pt/C, however the current stabilizes at significantly higher levels. The enhancement factor is close to 3 at the end of the experiment (20 min) independent of the potential (Fig. 4a-b). At PtBi(0.8)/C, there is a clear change in the shape of the chronoamperometric curves: the steep current drop at beginning of the experiment is significantly decreased at 0.4 V and it even absent at 0.6 V. Furthermore, the current densities decrease only slightly over the whole 1200 s experiment period resulting in a current density that is 7.5 times higher than the Pt/C current density at 0.6 V (Fig. 4b). The current density at 0.6 V is twice as large as in 0.4 V, which seems to indicate that the high Bi coverage can facilitate the desorption of the tightly bound gluconolactone formed at 0.6 V [6]. Similarly at 0.4 V, the high current density of PtBi(0.8) indicates that the dehydrogenated glucose and gluconate formed at low potentials are also more lightly bound to Pt. These results confirm that Bi modification can be used to significantly enhance Pt activity towards GOR in acidic conditions through a reduced poisoning effect.

In the neutral 0.05 M PBS, the situation is similar to the acidic case (Fig. S7c-d). There is strong deactivation of the Pt/C catalyst and this can be mitigated by low Bi adsorption and almost eliminated by high Bi adsorption. The notable difference is that in this case the maximum improvement is achieved at 0.4 V with PtBi(0.8) instead of 0.6 V, which performs 6.5 times better than Pt/C at the same conditions (Fig. 4c-d). This appears to be due to the activation of GOR as there is more OH^- available compared to acidic environment [6,7] facilitating the oxidation and removal of glucose electro-oxidation products. The current densities are high even with Pt/C and the relative enhancement gained from Bi decoration is thus decreased. However, the activity does also increase in all the conditions with Bi addition and enhancement factors are between 1.1 and 2.5.

In 0.1 M NaOH, both the current density values and its retention are significantly higher than in acid or neutral as expected (Fig. S7e-f). There is a small and rapid decrease of current density in the beginning of the measurement for Pt/C at 0.4 and 0.6 V but this is eliminated already with low Bi coverage. As in the neutral case, the highest enhancement factor is achieved at 0.4 V with high coverage PtBi(0.8) (Fig. 4e-f). The poisoning is weak even for Pt/C at 0.6 V and the difference in performance comes mostly from initial activity. So unlike in acid and neutral, Bi does not affect so much the removal of poisoning species than the intrinsic rate of the oxidation of d-gluconolactone species generated at 0.6 V in alkaline.

Finally, it can be seen from the smaller errors in the enhancement factors calculated from the chronoamperometric data (Fig. 4) compared to those calculated from the CV data (Fig. 3) that the chronoamperometric method is more reliable than CVs. This is most likely due to better removal of various GOR products by rotation from the vicinity of the electrode.

When comparing the enhancement factors from CV and chronoamperometric measurements, it is evident that studying the effect of Bi only from CVs would lead to underestimation of the effect of Bi adsorption. With chronoamperometry, the improvement in poisoning resistance can be appreciated fully during the longer time scale and reproducibility of the results are improved due to product removal through constant stirring. Under these conditions, the catalyst shows excellent potential for continuous electricity generation.

4 Conclusions

In this work, the effect of irreversibly adsorbed Bi to commercial carbon supported Pt nanoparticles on glucose electro-oxidation was studied. Bi was successfully adsorbed on Pt/C at a broad scale so that up to 90% of the Pt sites available for hydrogen adsorption were blocked. The Bi layer was stable to 0.7 V vs RHE in acidic solution and to 0.8 V vs RHE in alkaline solutions. In neutral phosphate buffer, Bi was not observed to etch from Pt even at 1.2 V vs RHE making the modified catalyst very robust and versatile at physiological pH.

The activity of the modified PtBi/C catalyst towards glucose electro-oxidation was tested in acidic (0.1 M $HClO_4$), neutral (0.05 M phosphate buffer) and alkaline electrolytes (0.1 M NaOH). In all of the cases, significant improvements compared to unmodified Pt/C both in activity and poisoning resistance were observed. The ratio of the glucose oxidation current densities between the modified and the unmodified electrodes measured from cyclic voltammograms was between 1 and 2 indicating clear improvement in activity in all the electrolytes. However, using chronoamperometry as the method the ratio increased to high values between 6 and 7 due to severe poisoning of the Pt/C electrode. Especially high Bi coverage (80%) improved the current density retention indicating that the adsorption of poisoning intermediates is weakened by Bi. The results show that irreversible Bi adsorption is a highly effective way to improve the activity and stability of a commercial Pt/C catalyst for glucose electro-oxidation over the whole pH scale. This robust catalyst makes electrochemical applications in energy conversion and glucose sensors more attractive and realistic.

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Supplementary Information

Activation of commercial Pt/C catalyst towards glucose electro-oxidation by irreversible Bi adsorption

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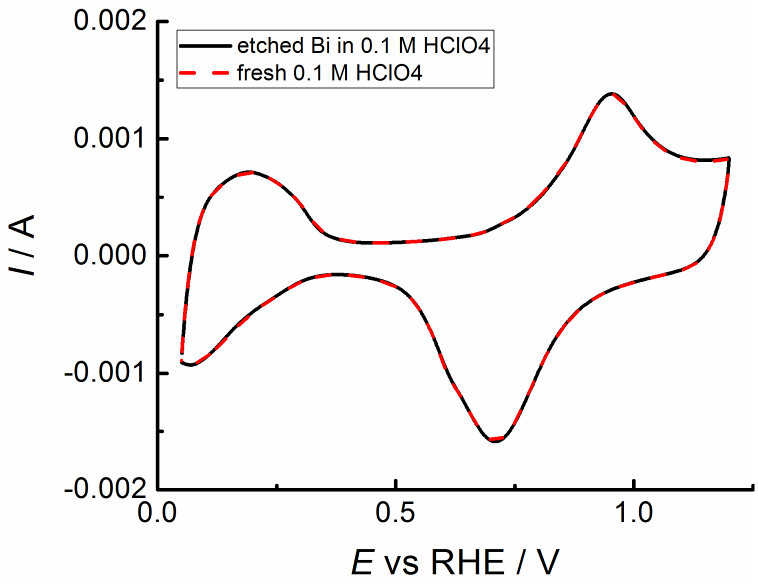

Figure S1. Cyclic voltammetry comparison of a PtBi(0.35)/C electrode in 0.1 M $HClO_4$, where Bi has been etched from coverage 0.87 to 0.35, and in fresh 0.1 M $HClO_4$ (0.02 V s^{-1}).

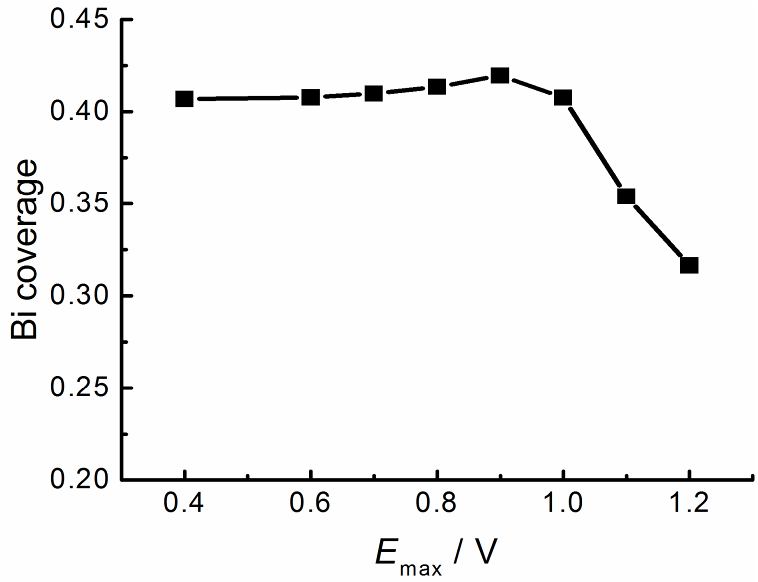

Figure S2. The Bi coverage evolution of PtBi/C electrode in 0.1 M $HClO_4$, when the electrode is cycled 50 times from 0.05 V vs RHE to a maximum potential noted on the x-axis (0.05 V s^{-1}).

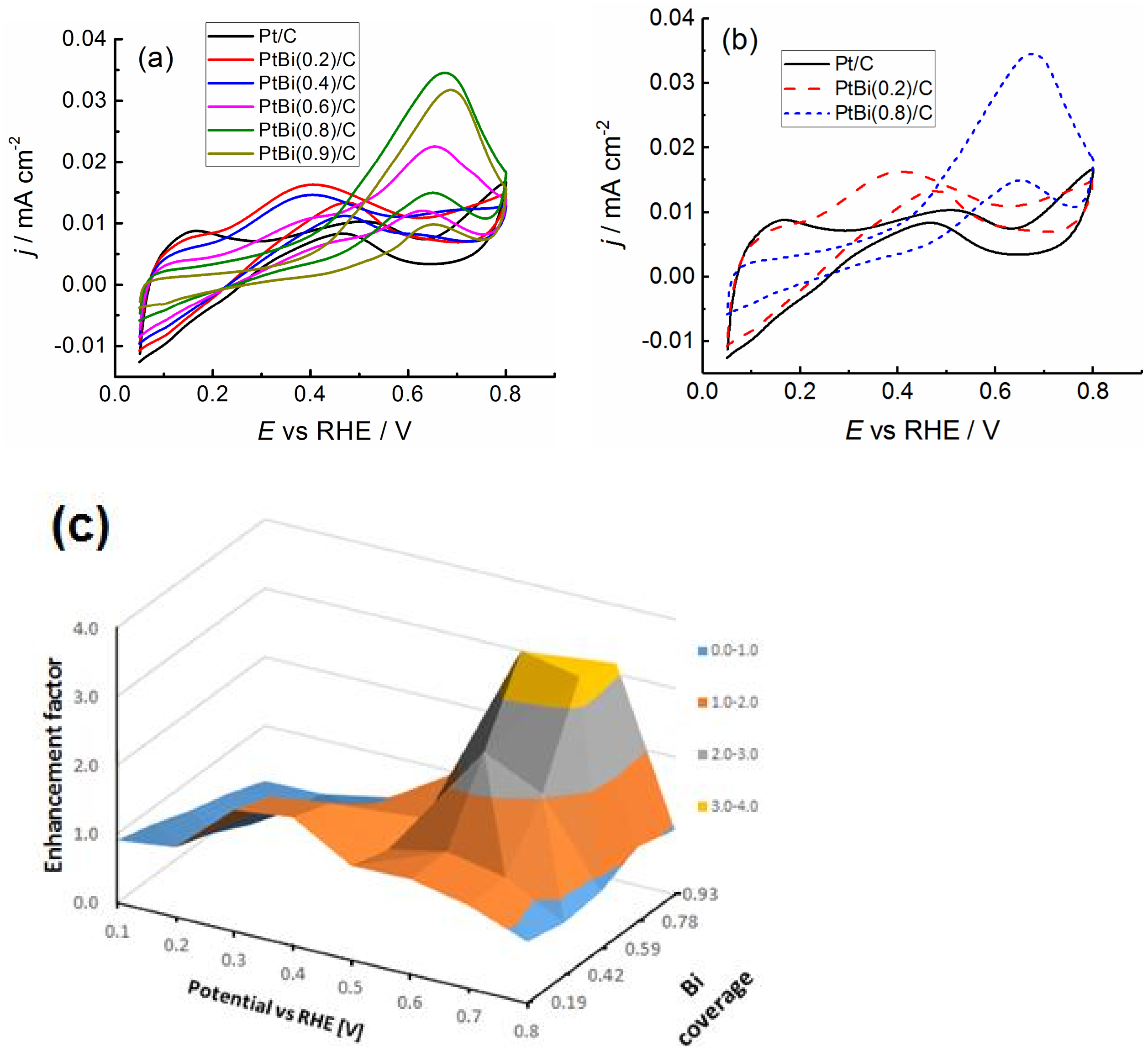

Figure S3. Comparison glucose oxidation activity in 0.1 M D-glucose solution and 0.1 M $HClO_4$ with different Bi coverages. (a) Cyclic voltammograms at all tested Bi coverages; (b) Selected coverages from (a) for easier comparison; (c) Plot of the enhancement of the current compared to the clean Pt/C electrode as a function of potential and Bi coverage. Data taken from the positive sweep in (a).

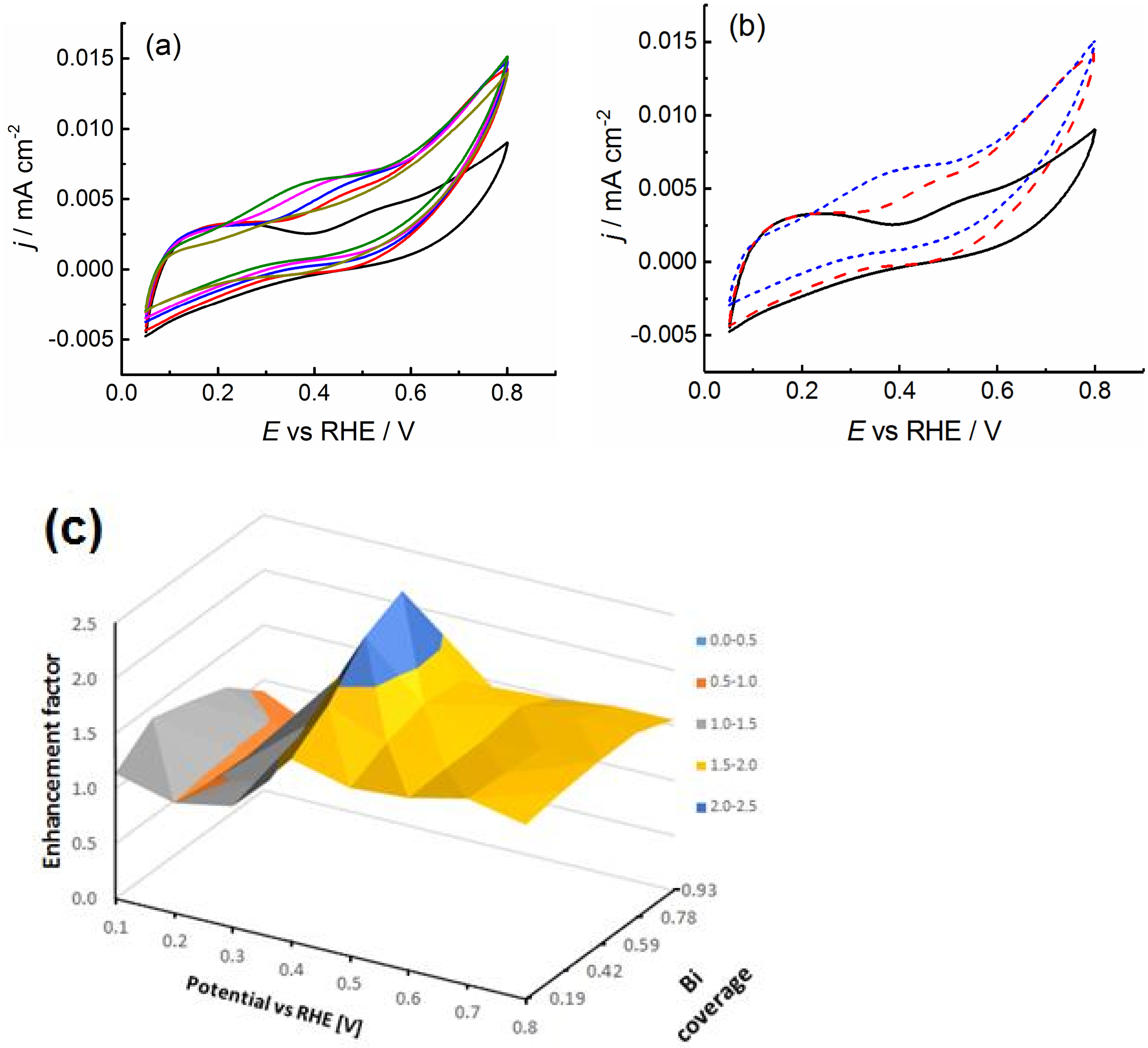

Figure S4. Comparison glucose oxidation activity in 0.1 M D-glucose solution and 0.05 M phosphate buffer (pH 7) with different Bi coverages. (a) Cyclic voltammograms at all tested Bi coverages; (b) Selected coverages from (a) for easier comparison; (c) Plot of the enhancement of the current compared to the clean Pt/C electrode as a function of potential and Bi coverage. Data taken from the positive sweep in (a).

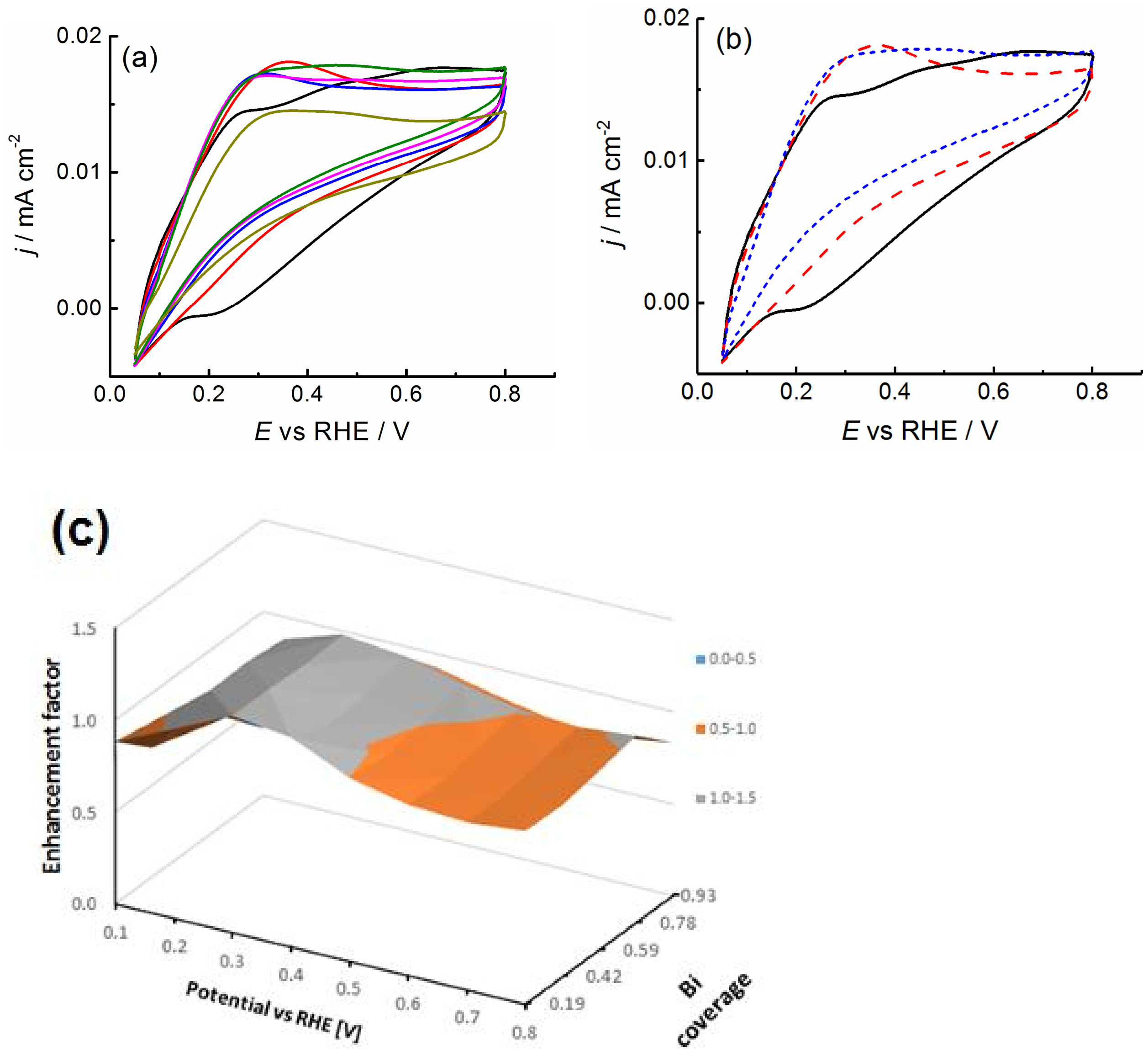

Figure S5. Comparison glucose oxidation activity in 0.1 M D-glucose solution and 0.1 M NaOH with different Bi coverages. (a) Cyclic voltammograms at all tested Bi coverages; (b) Selected coverages from (a) for easier comparison; (c) Plot of the enhancement of the current compared to the clean Pt/C electrode as a function of potential and Bi coverage. Data taken from the positive sweep in (a).

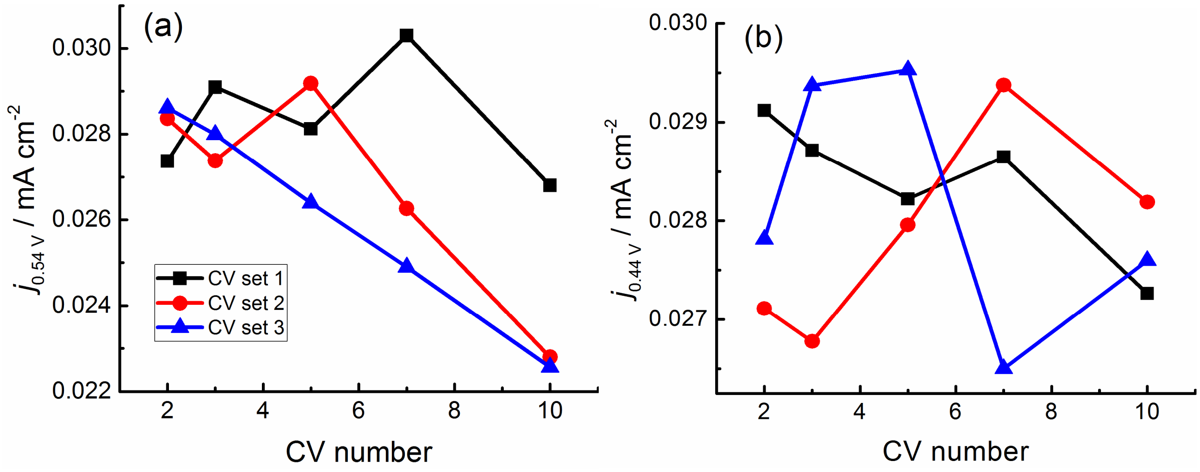

Figure S6. Comparison of currents in the positive sweep of CVs in 3 consecutive sets of 10 CVs from 0.05 to 0.9 V vs RHE in 0.1 M D-glucose solution and 0.1 M $HClO_4$ (a) Pt/C electrode at 0.54 V vs RHE. (b) PtBi(0.45)/C electrode at 0.44 V vs RHE.

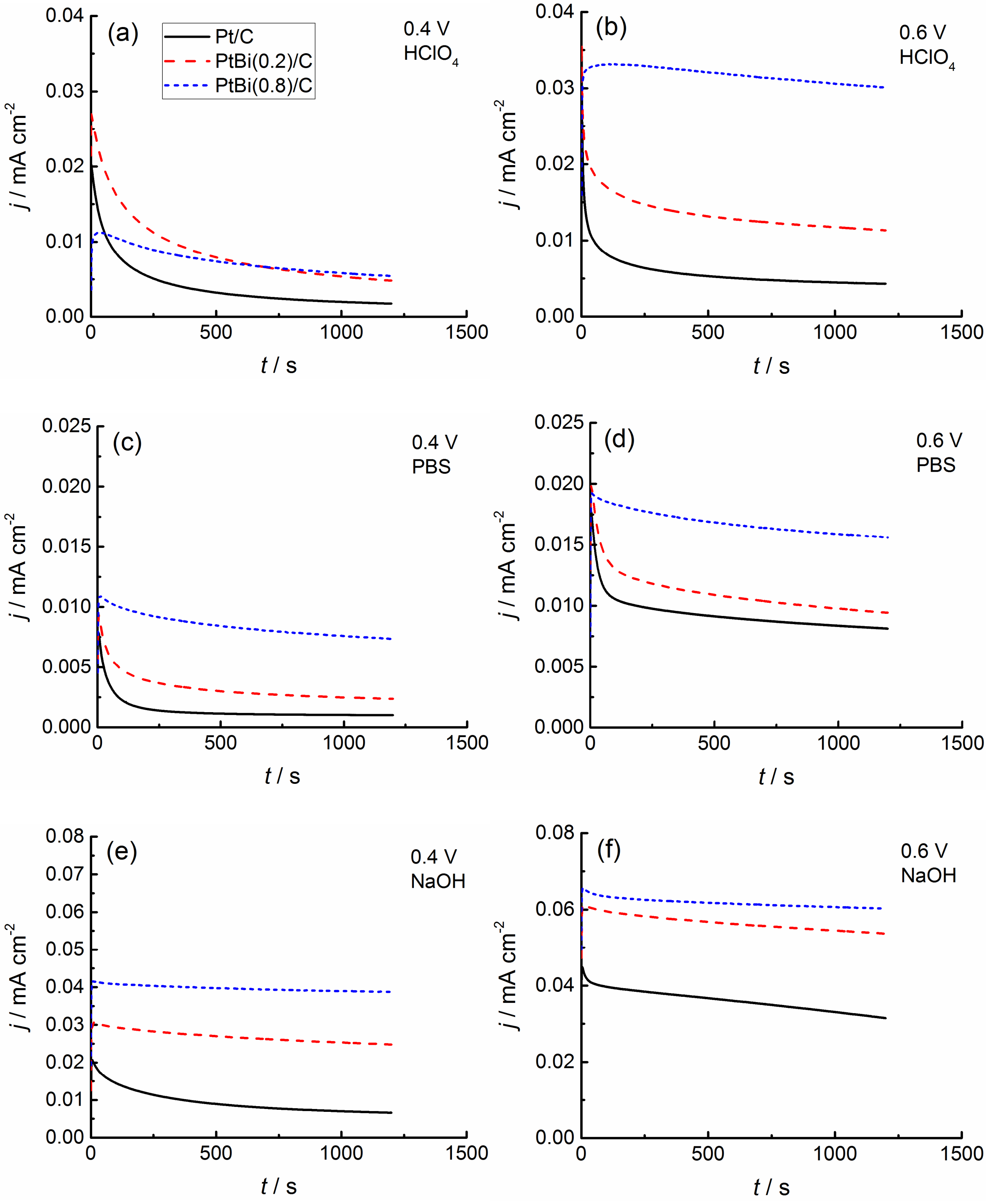

Figure S7. Chronoamperometric curves (1200 s) of Pt/C and PtBi/C electrodes with 100 rpm rotation in 0.1 M glucose and 0.1 M $HClO_4$ (a,b), 0.05 M phosphate buffer (pH 7) (c,d) and 0.1 M NaOH (e,f) at 0.4 V (a,c,e) and 0.6 V vs RHE (b,d,f). The measurement was preceded by electrode cleaning at 1.2 V vs RHE for 2 s.