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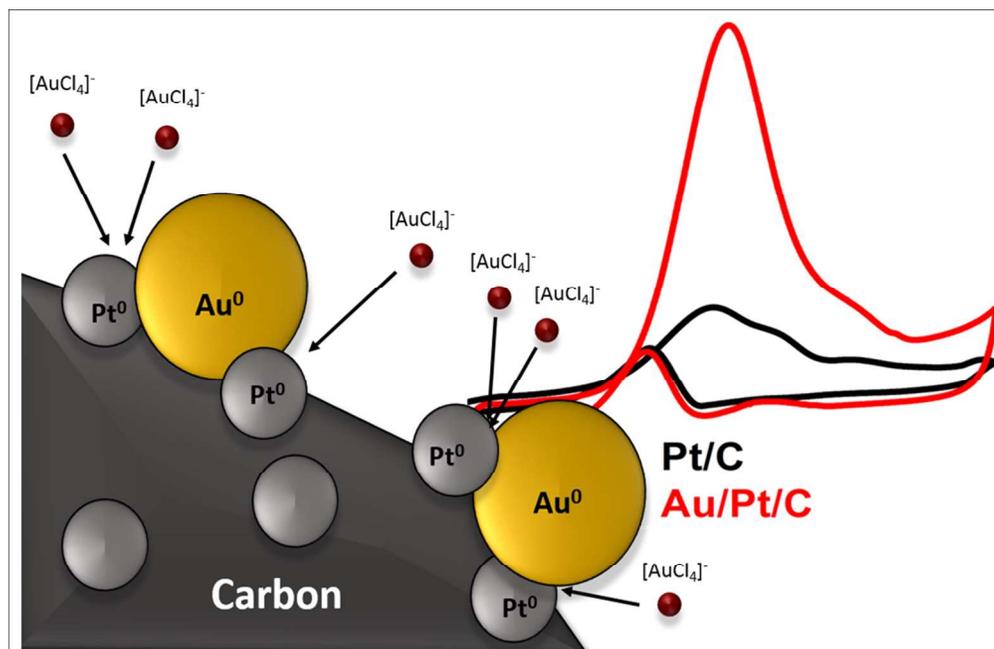
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Decoration of commercial Pt/C with Au via a simple solution process to improve electrocatalytic ethanol oxidation

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A simple approach to improve the electrocatalytic properties of commercial Pt/C

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Here we demonstrate that commercial carbon supported Pt nanoparticles react with [AuCl$_4$]$^-$ ions at room temperature to produce a highly active Au/Pt/C material with an ultralow coverage of elemental Au on the Pt nanoparticles that exhibits significantly enhanced activity for ethanol oxidation when compared to Pt/C.

The synthesis of Pt nanoparticles on carbon has been the subject of intense study for the last few decades. There has been a plethora of synthetic routes reported to achieve catalysts that are monodisperse on the nanoscale, exhibit excellent specific and mass activity, but are also stable in the long term. These attributes are critically important for fuel cell applications, in particular where the oxidation of small organic molecules is utilised.[1] Indeed there has been an equal research effort in minimising the use of Pt via alloying,[1b, 2] or complete replacement of Pt with less expensive metals and alloys[1a] or non-metal based catalysts.[3] In all of these approaches the new material of interest is benchmarked against mass produced commercial catalysts and demonstrated to be far more effective. However, the question arises as to whether these synthetic routes will be adopted for the commercial production of Pt/C catalysts on a large scale? An alternative approach to this problem would in principle be to introduce a simple protocol that increases the activity of the preformed commercial catalyst. Research in this area is far more limited and examples include impregnation of commercial Pt/C with metal phthalocyanines[4] or immobilisation on carbon fibrous mats to improve electrocatalytic activity.[5] It is well known that Au/Pt materials exhibit enhanced performance for a wide variety of organic molecule oxidation reactions such as formic acid, methanol and ethanol oxidation due to a bifunctional mechanism that alleviates surface CO poisoning[6] and has the added advantage of preventing dissolution of Pt during the oxygen reduction reaction.[7] Therefore, a simple way of modifying a commercial Pt/C catalyst with Au would, in principle, be highly beneficial. This option is explored here whereby simple immersion of a commercial Pt/C catalyst in a gold salt solution results in the formation of highly active Au/Pt/C materials that show

significantly enhanced activity for ethanol oxidation compared to the unmodified Pt/C catalyst.

The formation of Pt/C decorated with Au was achieved by immersion of 0.5 mg of Pt/C (20 wt%) in an aqueous solution of HAuCl$_4$ (1 mL) over a concentration range of 0.5 to 10 mM for 30 minutes. The resultant material was washed with water to remove unreacted HAuCl$_4$ (full details given in Supporting information). Illustrated in Figure 1 are cyclic voltammograms recorded for Pt/C (sample 1) and Pt/C after immersion in 0.5 (sample 2), 1 (sample 3) and 10 mM (sample 4) HAuCl$_4$. For Pt/C the response is typical for polycrystalline Pt[8] exhibiting on the positive sweep a hydrogen desorption region from -0.20 to 0.10 V, followed by the double layer region until ca. 0.70 after which oxide formation on Pt occurs until the end of the positive sweep. On the negative sweep the oxide is removed as illustrated by the broad peak centred at ca. 0.40 V, followed by a capacitive current until 0.10 V after which hydrogen is adsorbed on to the surface until the end of the sweep. Interestingly the hydrogen adsorption/desorption region is poorly defined with no evidence of the butterfly peaks associated with Pt single crystal electrodes,[9] commercially available bulk Pt electrodes[10] or electrodeposited Pt electrodes,[11] however behaviour of this type for carbon supported Pt nanoparticles has been observed previously.[12]
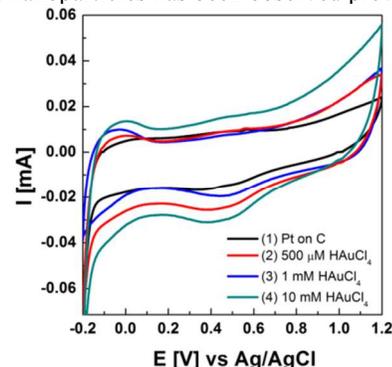

Figure 1: Cyclic voltammograms recorded at 50 mV s^{-1} in 1 M H$_2$SO$_4$ of commercial Pt on C (1) reacted with 0.5 mM (2), 1 mM (3) and 10 mM (4) HAuCl$_4$ for 30 min.

Once the Pt/C was treated in the $HAuCl_4$ solutions the cyclic voltammetric behaviour of the resultant material changed. It can be seen in all cases the magnitude of the overall response increased in comparison to unmodified Pt/C indicating an increase in surface area. What is even more fascinating is that the hydrogen adsorption/desorption region becomes more defined after this treatment. This is particularly unexpected as Au is inactive for hydrogen adsorption. There is also a slight shift to more positive potentials for the oxide reduction response at all treated electrodes indicative of a Au/Pt surface.[13]

Given that the cyclic voltammetric data does not irrefutably indicate the presence of Au, X-ray photoelectron spectroscopy (XPS) experiments were carried out for these samples (Figure 2). It is clear that Pt/C has been modified with Au as indicated by the peaks at 84.7 eV ($4f_{7/2}$) and 88.4 eV ($4f_{5/2}$) (Figure 2B) which are indicative of elemental Au.[14] Additionally the intensity of the Au 4f signals increase with increased concentration of $HAuCl_4$ used during the reaction. This is accompanied by a slight suppression in the intensity of the Pt $4f_{7/2}$ and $4f_{5/2}$ peaks at 71.3 and 74.7 eV whose peak positions are indicative of Pt^0.[15] From this XPS data, the percentage of Au on Pt can be calculated and was found to be 2.2, 4.9 and 5.4 % for Pt/C immersed in 0.5, 1 and 10 mM $HAuCl_4$ respectively.
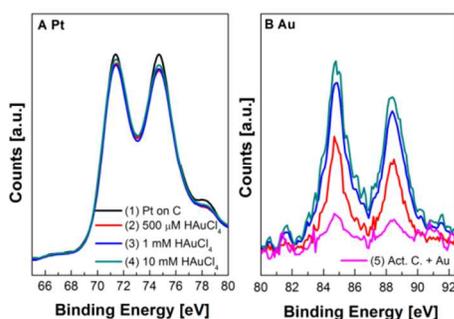

Figure 2: XPS analysis showing the (A) Pt 4f and (B) Au 4f core level spectra of Pt on C reacted with increasing $HAuCl_4$ concentrations and activated carbon reacted with $HAuCl_4$.

This indicates that the reaction is almost concentration independent above 1 mM $HAuCl_4$ and is limited by Pt/C and not the gold salt. The XPS data also does not indicate any alloy formation as the peak positions for Pt do not shift in the presence of Au and indicate that a phase separated Au/Pt bimetallic material has been formed. It is known that carbon contains surface oxide functional groups that may partake in redox reactions which could result in the deposition of metal on the carbon material.[16] Therefore a control experiment was carried out using activated carbon immersed in 1 mM $HAuCl_4$ to investigate this possibility. The XPS data (Figure 2B) indicates some formation of elemental Au on carbon but the amount is significantly lower than that observed in the presence of Pt and is further evidence that it is the Pt nanoparticles which are dictating the reaction. High resolution transmission electron microscopy (HRTEM) images were also taken of the Pt/C and Au/Pt/C materials (Figure 3). For Pt/C (Figure 3A and B), particles of ca. 5 nm in diameter are spread over the carbon particles with some evidence of agglomeration. However for Au/Pt/C, larger particles can be seen in addition to the smaller Pt particles that are decorating the carbon support (Figure 3C). At higher resolution (Figure 3D) it is clear that the larger particles are deposited on the underlying smaller Pt particles as well as being in intimate contact with many adjacent Pt

nanoparticles. A line mapping EDX experiment (Figure S1) confirmed that the larger particles consisted mainly of Au.
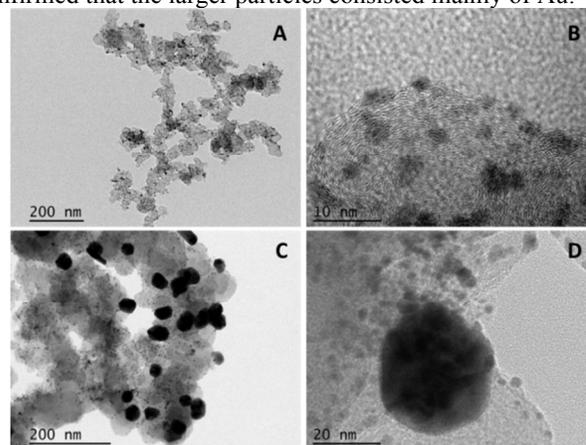

Figure 3: HRTEM images of (A and B) commercially available Pt on graphitised carbon and (C and D) the commercially sourced Pt on C material after immersion in 1 mM aqueous $HAuCl_4$ for a period of 30 min.

Given the synergistic effect often seen between two metals in electrocatalytic reactions, Pt/C and Au/Pt/C were utilised for the electrocatalytic oxidation of ethanol in alkaline solution. This reaction is particularly sensitive to AuPt materials as reported by previous studies from our group and that of others.[17] The results presented in Figure 4 show that Pt/C modified with only a small percentage of Au has a significant impact on the electrocatalytic activity for this reaction. For sample 1 with 2.2 % Au the onset potential does not shift but the magnitude of the response at -0.20 V (I_f) increased by ca. 1.9 times. For sample 3 with 4.9 % Au there is a dramatic increase in activity to ca. 4.2 times that of the unmodified Pt/C. However this trend does not continue for sample 4 with 5.4 % Au and the activity decreases but is still 2.2 times that of the Pt/C. In all cases for Au/Pt/C materials the anodic peak on the reverse sweep at -0.45 V (I_b) in comparison to the forward oxidation peaks is significantly less than that observed for Pt/C where the latter peak is generally attributed to the formation of surface contaminant species such as CO_{ads}. The ratio of the magnitude of the peak currents of these two features ($I_f:I_b$) is often used to compare the tolerance of catalysts to poisoning[18]. For the commercial Pt/C material this ratio is observed to be ca. 1.5 which increases upon the addition of Au up to values of 3.4, 4.6 and 5.9 for samples 2, 4 and 3 respectively. This increased tolerance to poisoning is well known for the Au/Pt system and is sensitive to the loading of Au on the surface of Pt.[17d] In this case it is observed that sample 3 (4.9 % Au) demonstrates the highest activity and tolerance to poisoning and that increasing the Au content further does not enhance performance. It should be noted that the ethanol oxidation data has been normalised to the electrochemically active surface area of the samples via determination of the charge associated with the hydrogen adsorption region on Pt and using the value of 210 $\mu C\ cm^{-2}$.[19] Therefore even though sample 4 shows a slightly higher surface area (Figure 1) its specific activity is reduced. A control experiment using activated C decorated with Au as mentioned previously, showed no activity for ethanol oxidation (Figure S2). The stability of the catalysts is shown in Figure S3 and indicates that the decay in current at Pt/C is far more rapid than Au/Pt/C indicating that the presence of Au on Pt ensures a greater tolerance to poisoning.
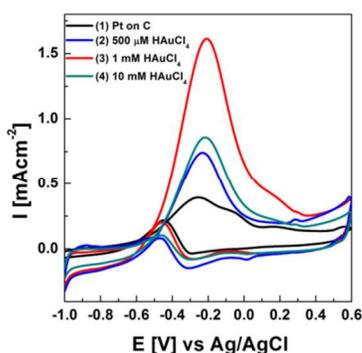
Figure 4: Cyclic voltammograms recorded in 1 M ethanol in 1 M NaOH at 50 mV s^{-1} obtained at Pt on C (1), Pt on C reacted with 0.5 mM (2), 1 mM (3) and 10 mM (4) HAuCl$_4$ for 30 min.

The mechanism by which Au is deposited onto Pt may originate via two processes. The standard reduction potential values for the Pt/PtCl$_4^{2-}$ and Au/AuCl$_4^-$ couples are 0.758 and 1.002 V respectively. Therefore there is a thermodynamic driving force for the galvanic replacement of Pt with Au, however from previous studies this reaction appears to be kinetically limited and does not occur on smooth Pt.[17b] Indeed to achieve Pt nanoparticles decorated with Au, a sacrificial Ag layer is often replaced by Au via a galvanic replacement process.[20] A disadvantage of this approach is that residual Ag may remain. An alternative view is that nanomaterials have sites on their surface which are easier to oxidise than the bulk metal. Previous work by Burke and others have shown that Pt can be oxidised at potentials lower than that thermodynamically predicted at the bulk material once the surface is activated either electrochemically or thermally.[8, 10, 21] For the more noble system of Au compared to Pt, we have shown previously that highly nanostructured electrodeposited Au as well as e-beam evaporated Au can be decorated with Ag, Pt and Pd when the surface has been shown to oxidise at potentials significantly lower than the bulk oxide formation process.[17a, 22] This was confirmed by Chung et al. in analogous studies with porous Au.[17c] However, the decoration of Pt with Au has only been reported for severely activated Pt electrodes.[17b] This is the first time that Pt nanoparticles have been shown to be capable of being decorated with Au via simple immersion in a gold salt without any prior activation. Evidence for the oxidation of Pt in the double layer region is shown via a small process at 0.57 V (Figure S4) which disappears once reacted with HAuCl$_4$ at a concentration above 0.5 mM. Further evidence that this process is limited by the participation of active sites is that only 5.4 % Au can be deposited on the surface, generally galvanic replacement processes of nanoparticles result in near complete replacement at these concentration levels of gold salt. At the Pt/C surface, in the presence of HAuCl$_4$, the deposition process relies on the mixed potential developed at the surface which will be sensitive to the nature of surface sites. Therefore in principle at this mixed potential the entire surface could be covered (including the carbon support), however this is not evidenced by the cyclic voltammetric data in Figure 1 which is indicative of a Pt surface or by the concentration of Au determined by XPS. The HRTEM data also shows that Au decoration is sparse and only occurs on specific groups of underlying Pt nanoparticles. Therefore it is assumed that the deposition occurs at the most active Pt sites and becomes limited. It also indicates that not all Pt nanoparticles are equally active for this deposition process. The question also arises whether electrons injected into the carbon support from the

oxidation of Pt active sites may have propagated laterally and provided a means for the deposition of Au nanoparticles. This is likely as the Au nanoparticles are deposited over numerous Pt nanoparticles and for growth to occur between Pt nanoparticles electrons must be continuously supplied through the support. However, it is clear from the cyclic voltammetric data in acid and the ethanol oxidation data that Au nanoparticles devoid of contact with Pt are not produced. If this were so there should be a distinct oxidation peak for ethanol oxidation at Au at more positive potentials of ca. 0.20 V vs Ag/AgCl (see Figure 3a in ref 17b) rather than the significant increase in current seen at -0.2 V (Figure 4). It is only through the intimate contact of Au and Pt that such an enhancement in current could occur.

Regarding the nanoparticles of ca. 5 nm diameter, it cannot be conclusively proved that they do not contain some Au even though HRTEM images (Figure S5) do not show any clear evidence of distinctive Au particles. Recent work by Clavilier[23] highlighted a critical point when Au electrodes were modified with Pt adatoms via electrodeposition from a solution containing a very dilute source of Pt ions. The resultant Au modified electrode showed electrocatalytic activity for the hydrogen oxidation reaction even when there was no evidence of Pt from cyclic voltammograms recorded in acidic electrolyte. Therefore the presence of adatoms of a second metal on the surface of a support metal has significant implications for electrocatalysis. In the work presented here adatoms of Au may also be deposited on the surface of the Pt nanoparticles that are beyond the capability of the TEM and the compositional mapping facilities used here. Indeed in Clavilier's work they stated that it was not possible to determine if it was single atoms or clusters of adatoms that constituted an active site.[23]

In summary the decoration of commercial Pt/C with a trace amount of Au via simple immersion of the catalyst in a gold salt results in a highly active electrocatalyst for ethanol oxidation. This approach opens up the possibility of decorating other commercial catalysts with metals that are not amenable to galvanic replacement and may lead to a route to generate single atom catalysts that are receiving much attention where single atoms or sub nanometre clusters are stabilised in a host matrix to both harness their activity and prevent their consumption.

Notes and references

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Electronic Supplementary Information (ESI) available: [Full experimental details, cyclic voltammograms for activated carbon in ethanol, EDX line maps, HRTEM images of Au/Pt/C]. See DOI: 10.1039/c000000x/

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