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Au/Pt nanoparticle systems in methanol and carbon monoxide electroxidation

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ABSTRACT

Different Au/Pt bimetallic systems have been synthesised by following the approach suggested by Brust. The nanoparticles have been anchored to glassy carbon surface through a place-exchange reaction involving dithiol molecules. The resulting modified electrode consists of heterogeneous nanostructured Au and Pt patchwork. The different nanoparticles systems developed have been employed for the electroxidation of methanol and carbon monoxide in alkaline aqueous media. The results show that the electrocatalytic activity of the bimetallic systems is enhanced with respect to the single monometallic NP systems.

1. Introduction

It is well known that it is often possible to improve the catalytic performances of a single metal by addition of a second metal, even in some cases in which this is on its own catalytically inactive [1–8]. As a consequence, bimetallic systems, under the form of bulk or nanostructured ones, are widely used in catalysis and electrocatalysis.

A catalytic action is necessary in order to achieve effective electroxidation of CH_3OH, which has been investigated in the past on different mono- and bimetallic systems, both in bulk and in nanostructured phases [9,10]. The overall process involves the adsorption of CH_3OH molecules on the electrode surface, followed by a complex sequence of reactions; different paths are possible, leading to the formation of different species on the surface. The formation of species poisoning the electrode is likely under most of the experimental conditions studied so far, CO molecules being the most clearly recognised. As a result, literature reports the investigation of the electrochemical behaviour of solutions only containing CO [10], in order to test the electrode behaviour with respect to this fouling species.

In order to improve the efficiency of the traditional Pt-based catalysts, the addition of Au to Pt has been suggested for effective CH_3OH [11,12], formaldehyde [13] and phenol [14] electroxidation, in conversion of solar into chemical energy [2], and in various selective gas-phase oxidations [15]. First studies involved the use of bulk metal alloys [16,17] or of a thin film of Pt on Au and vice versa, deposited by means of electrochemical and non electrochemical methods, e.g. by sputtering technique [18,19]. It is worth noticing that the phase diagram of the Au–Pt system exhibits a wide miscibility gap which, in principle, prevents from the formation of an alloy [20].

However, different scenarios have been outlined for the case of NPs, since the properties of the matter are, in general, quite different when the size of the crystals decreases down to few nanometers. In the case of NPs, most of efforts have been focused on the preparation of alloys, since highest intimate contact between Pt and Au atoms is claimed to be necessary in order to take advantage of synergic effects in (electro)catalysis [21–23]. In such a context, some papers report the formation of Au core|Pt shell and Pt core|Au shell structures [24–26]. A simpler approach consists in the preparation of a mixture of NPs of the two metals; under proper conditions, the Au and Pt cores can be deposited on a conductive support, resulting in close contact with one another. In such a modified surface both metals are also in contact with the environment, e.g. the solution phase in the case of electrocatalysis. This arrangement of the metal cores opens the possibility to enhance the electrocatalytic performance, with respect to the monometallic systems, taking advantage of bifunctional mechanisms, or even of 'ensemble' or electronic effects [9], similarly to what claimed in the case of alloys.

Surprisingly, only few papers deal with the preparation of mixtures of Au and Pt NPs [27–33]. In particular, only few of them deal with the relevant electrocatalytic properties, the most ones concerning the electroxidation of CH_3OH [27] and formic acid [34] or electroreduction of O_2 [27,31] in acidic media. Literature on

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similar bimetallic systems that considers alkaline aqueous solutions is even scarcer [30], although investigations in similar media are of key importance from a technological point of view, in particular in the development of direct alcohol alkaline fuel cells [35].

In the present work, Au, Pt, and Au–Pt systems have been prepared according to Brust's procedure, the bimetallic systems being obtained through co-reduction of the relevant metal salts [36] and grafted to a glassy carbon (GC) substrate through a place-exchange reaction [37]. The nature of the NP systems was checked by means of Transmission Electron Microscope (TEM) coupled with Energy-Dispersive Spectrometer (EDS) and UV–vis spectroscopy. Electrochemical tests have been performed to study the activation of the electrocatalysts and the catalytic activity with respect to CH_3OH and CO electroxidation in alkaline medium. The GC support constitutes an ideal choice, since it is inert with respect to the investigated species.

2. Experimental

2.1. Synthesis of the NPs

The Brust's procedure [36,38] was followed for the synthesis of monometallic and bimetallic systems, encapsulated inside an organic monolayer of thiols in order to control their growth and to prevent aggregation. In the case of ca. 2 nm size monometallic systems, $NaAuCl_4{\cdot}2H_2O$ (67.6 mg) or K_2PtCl_6 (82.6 mg) salts were transferred from an aqueous solution (10 ml) to a toluene phase (6 ml) containing a phase-transfer agent such as tetraoctylammonium bromide (TOABr, 137.8 mg). Encapsulating molecules, namely 1-decanethiol (DT, 0.12 ml), were added directly to the mixture under stirring. Subsequently, an aqueous solution (6.2 ml) of a reducing agent, i.e. $NaBH_4$ (323.9 mg), was also added to the mixture. The reaction was let proceed under stirring, at room temperature, for 3 h.

6 nm Au NPs were synthesised employing 206.9 mg of $NaAuCl_4{\cdot}2H_2O$ dissolved in 20 ml of water, 1071.7 mg of TOABr dissolved in 40 ml of toluene, 0.5 ml of DT and 750.9 mg of $NaBH_4$ dissolved in 50 ml of water. At the end of the synthesis, a thermal treatment at 180 °C for 1 h was performed in order to decrease the size distribution [39].

In the synthesis of the bimetallic Au–Pt NPs systems, the Au and Pt salts were in different relative molar ratio, namely 1:1 (49.2 mg of $NaAuCl_4{\cdot}2H_2O$ and 21.3 mg of K_2PtCl_6) and 3.5:1 (29.8 mg of $NaAuCl_4{\cdot}2H_2O$ and 37.9 mg of K_2PtCl_6), hereafter indicated as Au05Pt05 and Au075Pt025, respectively; the concentrations of the other species were similar to those previously reported for Au and Pt monometallic systems. The reaction was let proceed under stirring, at room temperature. The NPs were submitted to a thermal treatment at 180 °C for 1 h in order to narrow the size distribution [39].

At the end of synthesis procedures, the excess of DT and TOABr was removed by subsequent extractions with absolute ethanol and the purified NPs were re-dissolved in toluene.

2.2. Instrumentation

TEM images were taken using a JEOL 2010 instrument, equipped with an energy filter supplied by Gatan and an EDS system supplied by Oxford Instruments. Samples were prepared spreading some drops of a solution of NPs in n-hexane onto a carbon-coated Formvar® film on copper grids. These were dried in air for at least 10 min. The peak positions of Au, Pt and S in the spectra obtained with EDS are very close to one another. Hence, only a careful exam can lead to correct interpretation of the results. The analyzed samples were prepared paying attention at reducing the density of NPs on the TEM grids. Only if the NPs are far enough from one another, in fact, it is possible to determine the composition even of a single NP.

UV–vis spectra were acquired using a Perkin-Elmer Lambda 20 on NPs solutions in n-hexane (ca. 0.25 mg/ml).

Electrochemical tests were performed with an Autolab PGSTAT 12 potentiostat/galvanostat (Eco Chemie), in a conventional three electrode cell, at 25.0 ± 0.1 °C. The tests were performed in an aqueous solution either containing 5 mol dm^{-3} CH_3OH or saturated with CO and containing 0.1 mol dm^{-3} KOH as the supporting electrolyte, previously de-aerated by bubbling Ar through. During the measurements an Ar flow was maintained above the solution, in order to prevent O_2 dissolution. The auxiliary and the reference electrodes were a GC rod and a saturated calomel electrode (SCE), respectively. All potential values reported are quoted with respect to this reference.

2.3. Electrode preparation

The NPs were deposited onto a GC electrode by dipping it into a toluene solution containing NPs at a concentration of ca. 1 mg/ml, and 0.1 mol dm^{-3} 1,9-nonanedithiol, for 12 h. Before dipping, the electrode was cleaned using abrasive paper, then with alumina at different grain size (1, 0.3, 0.05 μm), and finally sonicated [11,40–42]. The GC surface is completely inert with respect to CH_3OH oxidation under our experimental conditions. Every measurement was repeated three times in order to verify the repeatability of the responses obtained.

3. Results and discussions

3.1. TEM and UV–vis spectra

The mean diameter and size distribution of the synthesised NPs have been estimated from TEM images (Fig. 1, Table 1). The local composition has been determined by means of EDS coupled with TEM. The change in the width of the sampling area of the EDS system has been achieved by changing the beam section: the 'mean'

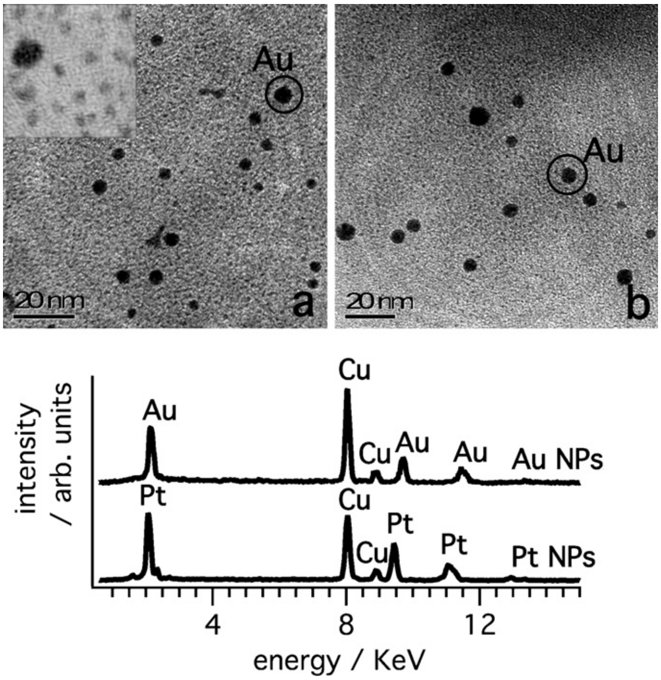

Fig. 1. TEM images of Au05Pt05 (a) and Au075Pt025 (b) NP systems together with the typical EDS spectra. The 15 nm × 15 nm inset in (a) shows a typical TEM image of Pt NPs in Au05Pt05 and Au075Pt025 samples, together with a Au NP.

Table 1
NPs TEM size in nm and relevant standard deviation (in brackets).

Sample	Au	Pt	Au0.5 Pt0.5	Au0.75 Pt0.25
Au metal cores	2.5 (0.5)		4.7 (0.7)	6.4 (0.8)
Pt metal cores		2.1 (0.3)	1.7 (0.3)	1.6 (0.2)

composition of the bimetallic system has been obtained using a wide beam section, while the composition of even one single NP could only be ascertained by a very narrow (down to few nm) beam section. The results lead to conclude that all the bimetallic samples under investigation are composed by a mixture of Au and Pt NPs, excluding the formation of a Pt/Au alloy. The pure Au and Pt systems possess mean diameter and size distribution similar to each other; on the other hand, in the case of bimetallic systems, the size of Pt NPs does not differ significantly from that of monometallic system, while a significant increase of the size of the Au NPs is observed. This increase is likely due to the thermal treatment.

UV–vis spectra of the monometallic systems are consistent with those reported in the literature [43]; in particular, Au NPs exhibit the well known plasmon band at ca. 500 nm, while Pt NPs do no show such an absorption. In the case of the bimetallic systems, the plasmon band is still present: the band of Au075Pt025 is more intense than that of Au05Pt05, due to the higher Au content (Fig. 2). In both cases the intensity is reduced with respect to pure Au system. Such a behaviour is in turn consistent with the formation of a mixture of NPs of different metals instead of an alloy: in the former case a progressive decrease of the plasmon band intensity at increasing the percentage of Pt is expected, while in the latter case a complete disappearance of the plasmon band has been reported when the Pt content exceeds 25–40%mol [8,44]. It is worth noticing that no signal due to Au(III), Au(I), Pt(IV) or Pt(II) species was recorded, leading to conclude that the reduction of the metal species is quantitative [45,46].

3.2. Grafting of the NPs

NPs encapsulated by thiols have been dissolved in a solution also containing 1,9-nonanedithiol molecules and grafted to the electrode surface through a place-exchange reaction leading to dithiol substitution for thiol. This approach has been followed to graft Au NPs on both GC and even glasses [40–42]. To our knowledge, such a strategy has not been used for Pt NPs; however, since Au and Pt surfaces covered by a thiol layer possess similar properties [47], it is reasonable to suppose that the place exchange reaction should be operative also for Pt NPs. This was checked by stably anchoring Pt NPs on GC. Furthermore, no attempt to contemporary deposit a mixture of NPs has been made so far by such a method; for similar reasons it seems quite reasonable that it is also effective when both nuclei are contemporary present in the bimetallic system. The electrochemical measurements reported below do constitute evident proof of the occurrence of the actual grafting of Au and Pt NPs at the same time.

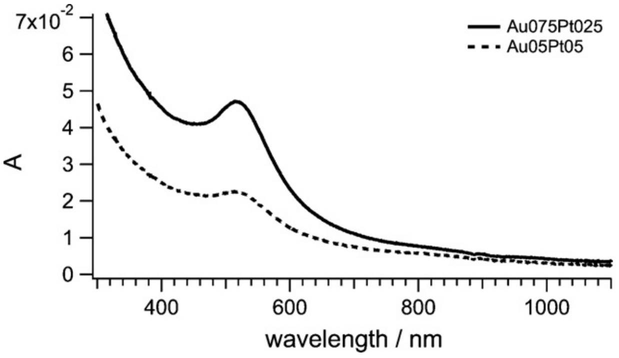

Fig. 2. UV–vis spectra of the bimetallic systems.

It must be evidenced that in the direct preparation of an NPs system surrounded by a dithiol monolayer by simply following the Brust's procedure undesired paths are well possible: both –SH groups are adsorbed at the surface of the same NP or massive insoluble aggregates form. It is worth noticing that the method of surface modification by NPs leads to the formation of a coating that covers completely the GC surface, as reported by the literature for Au and Au–Pt alloy NP systems [37]. However, the outmost surface exhibits different properties from bare bulk metal, thanks to the nanostructured texture.

3.3. Electrochemical tests

Electrochemical tests have been carried out in alkaline solution containing CH_3OH or CO. KOH electrolyte has been chosen, due to its importance in the realisation of alkaline fuel cells [35]. Keeping this in mind, as to CH_3OH, the conditions chosen for the present study are far from those usually employed in an electroanalytical context. On the other hand, the concentrations leading to the maximum efficiency in alkaline fuel cells do not always allow careful investigation of the electrocatalytic properties of novel electrocatalytic systems. For this reason, in order to investigate poisoning phenomena, a solution similar to that used in previous literature reports, i.e. containing 0.1 mol dm^{-3} KOH and 5 mol dm^{-3} CH_3OH, has been chosen; it should be however evidenced that quite different Au or Pt electrode systems are reported [48–50]. Owing to the differences in the electrode system, although the final goal of the paper lies in the study of Au and Pt bimetallic systems, investigations on the individual Au and Pt monometallic system were necessarily carried out, despite the large number of papers dealing with monometallic NPs [4,35].

In addition, a saturated CO solution has been employed to investigate the behaviour of the catalyst in the presence of this poisoning species, which forms as an intermediate in the oxidation process of CH_3OH.

Electrodes modified by a film of grafted NPs require an electrochemical 'activation' procedure in order to allow reliable and repeatable responses to be recorded. The activation consists in the positive polarisation of the working electrode in alkaline medium [12,51]. Activation can be carried out under either potentiostatic or potentiodynamic conditions. We choose adopting the latter procedure in the presence of CH_3OH or CO electroactive species, thanks to the possibility to 'monitor' the occurrence of the process by following the evolution of the relevant voltammetric curves. After each potential scan the circuit was opened and a short waiting time was elapsed, in order to restore the initial concentrations of the electroactive species within the diffusion layer. The current due to the oxidation of electroactive species, such as CH_3OH or CO, is very low over the first potential scan, so that no significant current peak is observed. In the subsequent potential scans, the current increases till gaining maximum catalytic activity.

The overall behaviour of the NP-modified electrodes in the case of both CH_3OH and CO electroxidation at the steady state, as well as during the activation process, can be explained by the Incipient Hydrous Oxide/Adatom Mediator model (IHOAM) [52–55] (see discussion hereafter). However, it is impossible to account for the increase of electroactivity of the bimetallic systems by identifying a detailed mechanism, including well-defined electronic or ensemble effects, only on the basis of electrochemical data. With this respect, a detailed spectroscopic study, well beyond the aim of the present paper, would be mandatory.

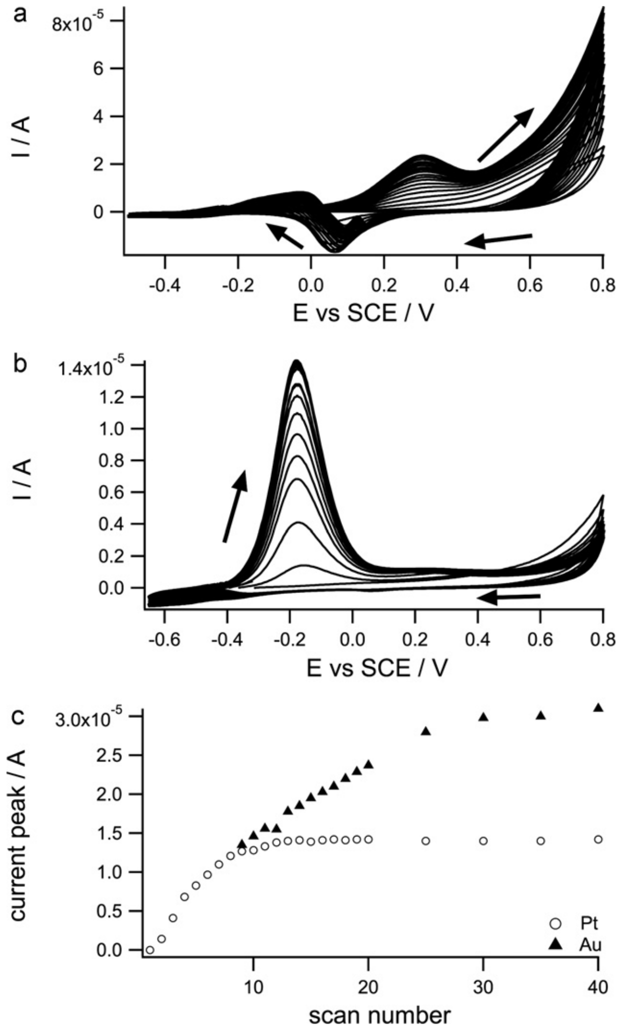

Fig. 3. Electrochemical activation of the GC electrode modified by monometallic NP systems. (a) Au; (b) Pt; (c) peak current values for the systems under study. 5 M CH_3OH, 0.1 M KOH, water solvent, 50 mV/s potential scan rate, first 20 scans.

3.3.1. *Au and Pt monometallic NP systems*

The voltammograms show the oxidation peak of CH_3OH, located at +0.30 V (Fig. 3a); the peak current progressively increases over the subsequent scans, reaching maximum height within ca. 40 scans. A further signal, poorly resolved from the solvent discharge, is ascribed to formation of Au oxides. In the backward scan, a reduction peak can be observed between +0.10 V and +0.20 V. These current signals should be associated to the reduction of the Au hydrous oxides formed in the forward scan. Finally, a small signal ascribed to CH_3OH oxidation is observed at ca. 0.0 V.

Quite a different behaviour is exhibited by the Pt NP electrode system (Fig. 3b). A fairly symmetric peak appears in the first forward potential scan, located at slightly negative potentials (−0.15 V). In the subsequent sweeps the relevant peak current increases up to reaching a maximum, then decreasing slightly up to a steady-state, after a few tens of scans. No response is recorded on the backward scan.

The peak current values ascribed to Pt and Au NPs, over subsequent potential scans, are reported in Fig. 3c. The peak current intensity is calculated only when the peak maximum can be clearly identified.

In the case of CO, the very first scan on the monometallic Au NP system does not show any significant signals, except for a very low anodic peak, located at +0.10 V, recorded in the backward scan.

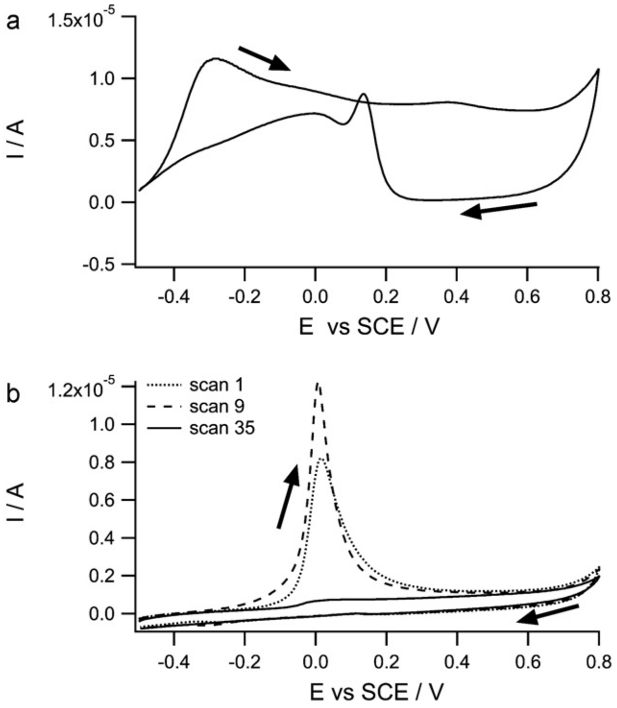

Fig. 4. Electrochemical activation of the GC electrode modified by Au (a), Pt (b) NP systems in 0.1 M KOH, CO saturated, aqueous solution, 50 mV/s potential scan rate.

It indicates that only a very small fraction of the metal surface can be reached by CO molecules by diffusion (i) through the alkyl monolayer and/or (ii) in the correspondence to its defects. The subsequent scans show a complex evolution of the whole system of peaks. The steady state, reported in Fig. 4a, is reached after ca. 30 scans.

Similarly to the case of CH_3OH, the reaction mechanism of CO electroxidation is not completely understood [35,54]. As a comment to this part of the study, it appears definitely risky to faithfully draw out an electrode mechanism for the processes occurring in correspondence to each voltammetric peak. In the case of CO, the voltammograms recorded result further complicated by the overlap of the responses due to CO to those due to Au hydrous oxides formation and reduction, on the backward scan.

The poisoning phenomena due to adsorption of CO at both massive and colloidal Pt surfaces are well known [56,57]. However, the behaviour of the Pt NP system has been tested by us for comparative purpose. In the voltammograms recorded only one peak can be observed at about 0.0 V in the forward scan (Fig. 4b). The peak progressively assumes a sharp, symmetric shape and after about 10 subsequent scans the peak current reaches the maximum value; then, it lowers more and more, the signal becoming hardly detectable after 30 scans. The electrochemical tests actually indicate a progressive poisoning of the electrode, taking place concomitantly to de-adsorption of the alkyl chains, i.e. in parallel to activation of the electrode surface.

3.3.2. *Au–Pt bimetallic NP systems*

The voltammetric behaviour with respect to CH_3OH, exhibited by the two Au–Pt NP systems considered, is shown in Fig. 5a and b. An anodic peak, quite broad in the case of Au05Pt05 system, with maximum current located at +0.25 V, appears in the forward sweeps; on the basis of the results discussed above, this peak can be ascribed to the electroxidation of CH_3OH on Au surface. After few potential cycles a second anodic peak appears at −0.15 V; the location of the relevant peak potential suggests that the process involved occurs at Pt NPs. The overall shape of the voltammograms

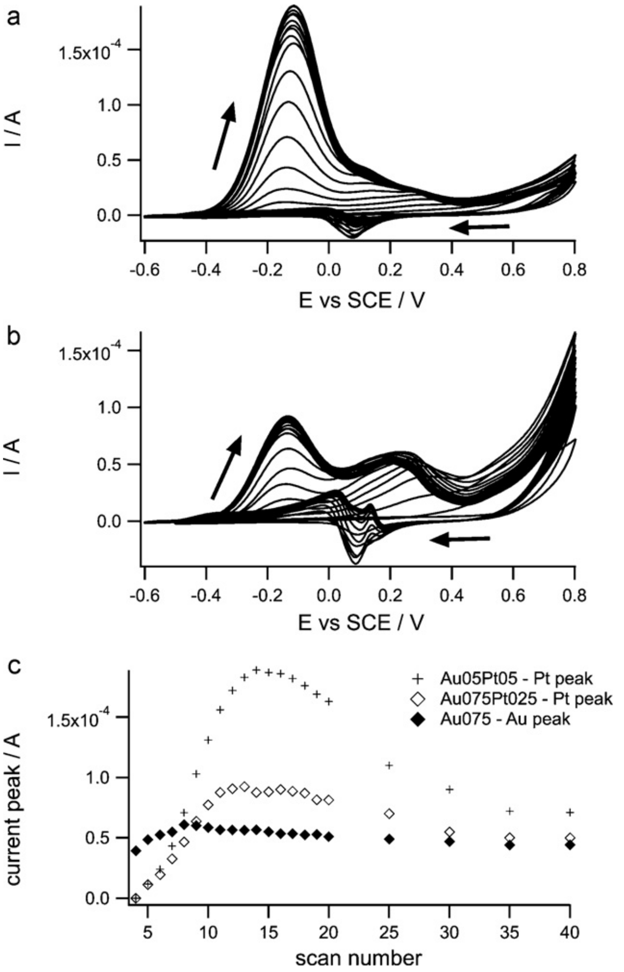

Fig. 5. Electrochemical activation of the GC electrode modified by bimetallic NP systems. (a) Au05Pt05; (b) Au075Pt05; (c) peak current values for the systems under study. 5 M CH_3OH, 0.1 M KOH, water solvent, 50 mV/s potential scan rate, first 20 scans.

recorded at the bimetallic electrode systems well coincides with the sum of the two traces individually recorded on the monometallic ones. Hence, electrochemical measurements support the conclusion that Au and Pt NPs can be grafted on the electrode surface through a place exchange reaction and that both metals are in contact with the solution, resulting electrocatalytically active.

Most interesting, the values of the peak currents (Fig. 5c) strongly depend on the composition of the solution used for the preparation of the NPs, and hence on the composition of the resulting bimetallic NP system. In the case of Au075Pt025 system, after ca. 10 scans the peaks ascribed to Pt and Au exhibit the maximum current, much higher than those of the individual Pt or Au systems, respectively. In the case of the Au05Pt05 system only the peak ascribed to Pt is clearly detectable, exhibiting the maximum value after ca. 15 scans; this value is even higher than that of Au075Pt025 system. At the steady state, i.e. after ca. 40 scans, the Au05Pt05 still behaves as the most effective system, the values of the current peaks resulting much higher than those recorded on the monometallic systems. A control experiment carried out depositing only 6 nm Au NPs show that the oxidation peak ascribed to CH_3OH in the forward scan, although resulting significantly less intense, is characterised by a location on the potential scale similar to that on 2.5 nm Au NPs. This behaviour is consistent with previous literature reports dealing with Au NPs possessing different size [58]. It is evident that a synergistic effect between Au and Pt NPs is operative in the case of bimetallic systems.

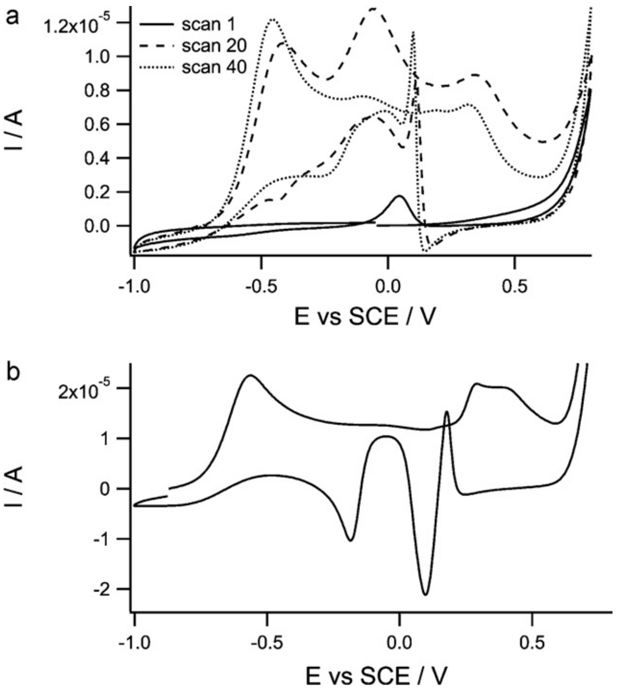

Fig. 6. Electrochemical activation of the GC electrode modified by Au05Pt05 (a), Au075Pt025 (b) NP systems in 0.1 M KOH, CO saturated, aqueous solution, 50 mV/s potential scan rate.

Similarly to the behaviour of the Au–Pt NPs activated in CH_3OH solution, the responses of the modified electrodes activated in CO-saturated solution well account for the presence of both Pt and Au on the surface of the electrode (Fig. 6). The evolution of the peaks over the subsequent potential scans and the steady-state voltammograms are similar to those shown by the Au monometallic NP system. However, a shift of the onset of CO electroxidation is observed: pure Au, Au05Pt05, Au075Pt025 systems exhibit a peak located at −0.28 V, −0.37 V and −0.55 V, respectively, the maximum peak current value being observed in the case of Au075Pt025 system. It is evident that a synergistic effect between Au and Pt NPs is operative also in this oxidation process. In addition, one peak at −0.05 V in the backward scan can be observed during the activation in the case of Au05Pt05: the peak current reaches a maximum and then decreases up to complete disappearance of the signal. This behaviour can be explained by a progressive poisoning of Pt during the activation process, in agreement with what observed in the case of the electrodes modified with Pt monometallic NP system.

4. Conclusions

The data allow us to conclude that the concomitant presence of Au and Pt metal cores in close contact with each other actually enhances the electrocatalytic activity toward the CH_3OH and CO oxidation, with respect to the single monometallic NP systems. Although a complete dampening of poisoning effects is not achieved, the deactivation of the electrode surfaces during CH_3OH and CO electroxidation seems to be significantly reduced with respect to the case of the Pt monometallic system. The composition of the starting NP mixture significantly influences the electrocatalytic behaviour: Au05Pt05 and Au075Pt025 NP systems are more active toward CH_3OH and CO electroxidation, respectively.

The approach followed to the preparation of Pt and Au NPs bimetallic systems can be extended to other metals possessing a miscibility gap, i.e. to metals whose relevant alloy formation is precluded both in bulk and under NP form.

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