Supported Binary and Ternary Nanoalloy Nanoparticle Catalysts—A Green Processing Approach using the Leidenfrost layer as Nanoreactor

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Abstract

When a nanocarbon substrate is heated between 300 °C and 320 °C that is slightly above the Leidenfrost temperature and subsequently quenched in an aqueous solution containing a mixture of noble metal ions, a high density of nanoalloy nanoparticles (NPs) form on the surface. Large surface areas can be decorated in this way by nanoalloy NPs of the system (Au, Pt, Pd). Both binary AuPt, AuPd and PtPd as well as ternary nanoalloys are obtained. The chemical composition of the nanoalloys can be tuned by varying the ion mixture ratio of the solutions. The simultaneous reduction of the noble metal ions on the surface occurs without the need of any reducing agent, presumably owing to charge transfer from ionized species during the quenching process. The method yields nanocarbon-supported, highly adherent nanoalloy NPs, is materials efficient and cost effective because only the surface is modified with the costly noble metals. The supported nanoalloy NPs are exemplary applied to the electrooxidation of methanol and formic acid in acidic solutions, and show an overall high performance.

1. Introduction

The performance of noble metal catalysts may be boosted by designing layered nanoparticles (NPs) with different metals [1], e.g. core shell NPs. Based on density functional theory computations, the mechanisms underlying the enhanced catalytic activity, e.g. for oxygen reduction reaction (ORR) catalysts, rely on the catalyst’s surface electronic structure being affected in a way that binding energy of oxygen and reaction intermediates to the catalyst’s surface sites is mitigated [2, 3]. Both compressive stress as it arises from large lattice mismatch between the underlying and noble metal, and ligand (formation of a Pt-skin on solute enriched under-layer) effects are thought to affect the electronic structure of the active metal, e.g. of the Pt-over-layer, in the desirable way [4]. Designing core-shell structures with few atomic layers of the active catalyst on top of a lesser noble metal may not only enhance performance but could also depress precious metal cost. However, at the exception of few intermetallic compounds between Pt and rare earths, chemical stability of the underlying metal under specific catalytic reaction conditions is not often fulfilled for most transition metals, and constitutes the main limiting factor to the widespread use of core-shell NPs catalysts [2–4].

Metal alloy nanoparticles (MANPs) afford a powerful alternative to elemental NPs in a plethora of applications. The growing interest in MANPs is largely motivated by their peculiar and, in general, more interesting property spectrum than the participating monometals (MoM). Whether in catalysis, plasmonics, or sensing, the performance of MANPs was reported to be superior to that of MoM (see the comprehensive reviews by Gilroy et al and Ferrando et al [5, 6]). In the case of noble metal catalysts, the drive to reducing the amount of expensive metals such as Pt has boosted the search for alloys that combine cost-effectiveness with better catalytic performance and long-term stability [7–10].
The formation of alloys is a natural tendency in the majority of metal systems which in terms of thermodynamics is driven by the exothermic free energy of mixing, e.g. when a heterostructure of MoM is heated to a sufficiently high homologous temperature \( (T/T_m) \), where \( T_m \) is the melting temperature of the metal with the lowest melting temperature) to drive solid-sate diffusion an alloy, a range of alloys or intermetallic compounds form, depending on the system, the annealing temperature and time. Intuitively MANPs may then be processed if one can deposit MoM–NP heterostructures followed by annealing as reported in Reference [11], where a nanolithography approach and physical vapor deposition was advantageously used to fabricate binary and ternary alloy NP arrays on a substrate. Other processing methods for MANPs are summarized in the review articles by Gilroy et al [5] and Ferrando et al [6]. But the most widely used of them is certainly the co-reduction in solution which presents the advantages specific to this method, such as the possibility to tune chemistry and geometry. Co-reduction in a solution of mixed ions is most widely used to generate bimetallic NPs or alloys, and draws advantage from the metal species being mixed at their smallest elementary states. However, depending on reducing agent and the reduction potentials of the participating ions, core-shell (when one of the metal ions has smaller reduction potential than the other), bimetallic (e.g. when the two metals form an interfacial zone but do not mix to an alloy) or solid-solution structures may form [5, 6], although there are also different strategies, e.g. using surfactants, stabilizers, refluxing etc, to influence the structure in the one or the other way. Reviews of the different methods so far reported may be found in references [12–14].

While co-reduction is certainly a powerful method for synthesizing multimetals and nanoalloys with different dimensions and morphologies, it nevertheless requires lots of chemicals, and presents drawbacks related to the low yield and the inherent difficulty of scaling-up to devices that require some sort of assembly of NPs on a substrate which is not an easy task because it entails filtration, functionalization of particles and substrate, etc (e.g. see the review articles [15, 16]).

The issues above were the main impetus of this work to seek developing an alternative approach that would allow easily and rapidly modifying a substrate surface with noble metal and nanoalloy NPs. The primary aim was to fabricate supported catalysts in a one-step processing route, while making use of as less chemicals as possible. Recently [17], we reported a unique method for the surface modification with noble metal nanoparticles (NMNPs) from aqueous solutions dispensing with any reducing agent. We first start with modifying the substrate surface with a layer of single walled carbon nanotubes (SWCNT) or bundles thereof, heat-up this surface to a temperature in the range of 300 °C and subsequently quenching it in the aqueous solution of the noble metal ion, e.g. a solution of \( \text{H}_2\text{PtCl}_6 \). Complex reactions that possibly involve water ionization and charge transfer to the metal ions at the interface with the SWCNT were thought to be responsible for noble metal ion reduction at specific sites on the CNT thus leading to tightly adherent nanoparticles on the surface. Herein we explore the fabrication of nanoalloys from mixtures of aqueous ionic solutions, and the extent to which the alloy composition may be controlled by adjusting the molar ratios of the participating ions.

It will be demonstrated in the course of this work that the method outlined above is very well suited to the processing of binary nanoalloys with tunable composition. It will also be shown that the method can be extended to ternary alloy NPs with outstanding electrocatalytic activity. There are undeniable advantages of the present method in comparison to co-reduction using reducing agents. The first one is the rapid reaction because the surface is modified within minutes, secondly large surfaces, e.g. for scaling-up, can be modified and thirdly high materials efficiency is achieved because only the surface is modified with the costly catalysts.

In the following, emphasis is placed on noble metal systems with complete miscibility at high temperature (formation of continuous solid-solutions). These include Au–Pt, Au–Pd and Pd–Pt as well as the ternary system Au–Pt–Pd. The phase diagrams of these systems in the bulk state can be found in References [18–20]. The substrates were porous nanocarbon-MWCNT composites supported on stainless steel that are subsequently modified with a layer of SWCNT as indicated in a previous report [17].

2. Material and methods

2.1. Substrate preparation

Etched and cleaned mill-finish stainless steel substrates were dip coated in a precursor solution consisting of 15 wt. % Polyvinylidene fluoride (PVDF), 12 wt. % Ammonium nitrate \( (\text{NH}_4\text{NO}_3) \) and 1 wt. % Multi-walled carbon nanotubes (MWCNT) in \( \text{N}_2\text{N}-\text{Dimethylformamide} (\text{C}_3\text{H}_7\text{NO}) \). The porous PVDF-MWCNT-nanocomposite films obtained were pyrolysed at 550 °C under nitrogen atmosphere, yielding porous nanocarbon-MWCNT-nanocomposite films. A detailed process description can be found in our earlier work [21, 22].
2.2. Surface modification and nanoalloy fabrication

The substrates with the porous nanocarbon-MWCNT-nanocomposite films were heated on a hot-plate to 310 ± 10°C and directly transferred to an aqueous solution of PEG functionalized SWCNTs to achieve a SWCNT modified surface [17]. Surface modification with noble metal NPs followed a similar procedure where the SWCNT modified substrates were heated again and transferred to the aqueous solution of the noble metal ions or a mixture thereof. Aqueous solutions of 2 mM of HAuCl₄, H₂PtCl₆, and K₂PdCl₄ were used for the processing of MoM NPs. For Au-Pt and Au-Pd alloys-NPs the 2 mM solutions were mixed with increasing ratios of Pt or Pd-solutions of 1:1, 1:2, 1:3 and 1:4. For Pt-Pd alloy-NPs the solutions of 2 mM of H₂PtCl₆ and 2 mM K₂PdCl₄ were mixed with increasing ratios of Pt-solution of 1:1, 1:2 and 1:4. For Au-Pd-Pt alloy-NPs the 2 mM of HAuCl₄, K₂PdCl₄, and H₂PtCl₆ were mixed with the ratio of 1:1:3 or 1:1:2. The solution mixtures and the resulting alloy composition determined from x-ray diffraction patterns using Vegard’s law, except for the ternary alloys where the composition was determined by energy dispersive x-ray spectroscopy, are summarized in the table S1 (available online at stacks.iop.org/NANOX/2/020013/mmedia) (Supplementary Material). Additionally, surface modification of Ni-TEM meshes was performed especially for the scanning transmission electron microscopy (STEM) investigations. For this purpose, Ni-TEM meshes were fixed on the stainless-steel substrates and the same procedure as above was applied to them.

2.3. Characterization

For structural analysis x-ray diffraction (XRD, XPert Pro diffractometer PANalytical, Holland) was performed in grazing incidence diffraction mode with constant θ = 1° using monochromatic Cu Kα radiation with λ = 1.5418 Å and a scanning range between 10° and 90° (2θ). The device has a full width to half maximum resolution of 0.03°. XRD data was evaluated using Lorentzian peak deconvolution, Bragg’s law, Scherrer-Formula and Vegard’s law. The microstructure and morphology were characterized with a high-resolution scanning electron microscope (SEM Ultra Plus, ZEISS, Germany) operating in the secondary (SE) and energy selective backscattered (ESB) electron modes. The SEM is also equipped with a STEM detector and energy dispersive x-ray spectroscopy (EDS) package (INCAx-ac, Oxford Instruments, UK). High resolution SE and ESB images were obtained with 2 kV acceleration voltage whereas the STEM investigations were conducted with 25 kV.

An electrochemical workstation (ZAHNER IM6e, Kronach, Germany) was used for cyclic voltammetry measurements. The electrochemical experiments were performed in 0.5 M H₂SO₄ in a three-electrode set-up with a Pt mesh and HydroFlex (reversible H₂ reference electrode) as the counter and reference electrodes, respectively. For methanol and formic acid electro-oxidation, 0.5 M H₂SO₄, i.e., the reduction region of 543, 493 and 424 μC cm⁻² as the charge density associated to the reduction of oxide species for pure materials, Pt, Au and Pd, respectively) [23, 24].

3. Results and discussion

3.1. Morphology and elemental analysis

3.1.1. Binary Au-Pt-, Au-Pd- and Pt-Pd-nanoalloys

SEM micrographs of the particle morphology are displayed in figure 1. Figure 1(a) is an overview of the surface topography with the porous nanocarbon surface, the network of SWCNT bundles and the AuPt nanoparticles, in this case for an Au:Pt solution ratio of 1:1. We discern larger particles in the size range from 20 to 100 nm, which exhibit a rough morphology, and very small ones densely decorating the SWCNT, figures 1(a) and (b). The larger particles seem to be composed of smaller ones as can be seen in the high-resolution micrograph, figure 1(b). EDS analysis and corresponding line scans, figure S1 (Supplementary Material), of these particles indicate the presence of platinum and gold, although it cannot be ascertained that individual particles in the cluster consist of an AuPt-alloy due to the well-known specific limitations of EDS-analysis for which the area sampled may be a manifold of the particle diameter. More evidence is obtained by x-ray diffraction to be discussed below. When the Au:Pt solution ratio decreases no noticeable change in the particle morphology could be observed.

A similar procedure to the previous one has been adopted for Au-Pd and Pt-Pd alloys. In principle, the particle morphology is very similar to Au-Pt-NPs, except for larger average particle size for both nanoalloys. As
mentioned before the larger particles are composed of an agglomeration of smaller ones conferring to the
particle a rough morphology. Supplementary figures S2 and S3 show the EDS analysis with the corresponding SE
micrographs of AuPd and PtPd alloy.

3.1.2. Ternary Au-Pt-Pd-nanoalloys
The ternary nanoalloys are prepared from an aqueous solution containing a mixture of 2:1:1 or 3:1:1 parts of
individual 2mM solutions (see the experimental section, 2.2). Additionally, Ni-TEM meshes modified with
ternary nanoalloys were investigated using the STEM modus of the SEM to examine the morphology in detail.
Figures 2(b) and (c) show bright and dark field STEM micrographs of particles whose morphologies suggest
bigger particles composed of smaller ones and a large number of very small ones decorating the SWCNT. The
dark field micrograph, figure 2(c), suggests a homogeneous contrast pointing to the monophase nature of
the NPs.

The particle morphology is very much the same as for the binary nanoalloys, but the particles definitely
contain Au, Pt and Pd with the predominance of Au, as depicted in figure 3, which shows EDS point analysis and
an elemental line scan profiles with the corresponding SE micrograph. It is possible to increase Pt or Pd just by
increasing their concentration in the solution. As indicated above, XRD is required to ascertain that the particles
effectively consist of an alloy.

3.2. XRD studies
A series of substrates were modified with Au-Pt, Au-Pd and Pd-Pt using solutions with different molar ratios of
Au:Pt, Au:Pd and Pd:Pt, and subsequently analyzed using grazing incidence (GI) XRD. Reference samples of
substrates modified with the MoM Au, Pt and Pd were also analyzed under the same conditions. The metallurgy
of the systems above is rather simple with the formation of continuous solid solutions at high temperatures.
Upon cooling the systems show a miscibility gap (case of Au-Pt and Pd-Pt) and long-range ordering (case of Au-
Pd) [18, 19]. Because the nanoalloys form at fairly low temperatures we may expect them to be disordered,
though surface enrichment with a specific component may be expected, and is indeed inferred from the
electrochemical investigations presented below. For all the investigated alloy compositions, the XRD patterns
yield for each hkl only one diffraction peak that indicates the formation of an alloy (or compound), as

Figure 1. Secondary electron (SE) micrographs of porous nanocarbon-MWCNT-composite films that were modified with SWCNT
and subsequently with Au-Pt alloy-NPs (a) is an overview showing densely distributed particles and SWCNT bundles. Notice that the
particles are also distributed in the pore cavities; (b) is a higher magnification micrograph showing the morphology of individual-NPs
where larger particles seem to be composed of smaller ones.
exemplified with the 111 reflection for selected alloy compositions, shown in figure 4(a). Further, the lattice constant of continuous solid solutions is supposed to follow Vegard’s law that indeed was reported for bulk materials of the alloys above [20]. Figures 4(b)–(c) summarize the results obtained for the binary alloys and shows that Vegard’s law is well obeyed and that nanoalloy composition can be tuned in a wide range. It should be pointed out that XRD affords right in the present case (NPs supported on a substrate) a precise enough method to determine disordered alloy NP composition, as it allows probing a large sample area, precluding any substrate effects, in contrast to other methods such as EDS. The ternary systems also yield only one hkl peak that underscores the formation of nanoalloys. From the lattice parameters alone obtained, 398.4 pm for the Pt10Pd43Au47-NPs, it is not possible to infer one specific composition but rather a range of alloy compositions, according to the isoparametric phase diagram reported in reference [20]. Complementary microanalysis, despite its caveats, may help narrowing the composition range. Table S1 (Supplementary Material) summarizes the results obtained with both XRD and EDS methods. The mean particle size calculated using the Scherrer formula is also shown in table S1. Au and Pd-NPs as well as PtPd-NPs have the highest mean particle size of approximately 20 nm whereas for Pt-NPs and the other nanoalloys mean particle size ranges from 9 to 4 nm are obtained.

3.3. Discussion of the formation mechanisms

The results above demonstrate that our processing method allows easy and rapid modification of a substrate surface with noble metal nanoalloys of varied composition dispensing of any reducing agent. Before describing the advantages of these nanoalloy NPs as electrocatalysts we should now briefly discuss their formation mechanisms.

When the substrate is quenched from 300 °C, which is slightly above the Leidenfrost-temperature, into the aqueous solutions of the noble metal ions we expect a Leidenfrost vapor layer to form at the substrate-solution interface. Depending on the amphiphilic properties of the substrate surface, the vapor layer may remain stable to fairly low temperatures (highly hydrophobic surfaces) or eventually rapidly collapses (case of hydrophilic
surfaces) through bubble evolution leading to rapid cooling of the substrate [25, 26]. Further, in a recent paper water ionization in a levitating Leidenfrost drop was reported as the main mechanism responsible for Au-ions reduction [27]. More recently, we have shown in a preliminary work that quenching of a SWCNT modified substrate from 300 °C into an aqueous solution of H₂PtCl₆ resulted in the formation of finely dispersed Pt-NPs over the whole substrate surface without need of any reducing agent [17]. We purported that water ionization processes at the interface between the vapor layer and the substrate could be responsible for Pt-NP formation. In figure S4 (Supplementary Material), a photograph of a nanocarbon film after surface modification with Au-NPs from an aqueous solution is shown, where surface appearance changes to yellowish, denoting the formation of a high density of Au-NPs, is clearly seen. The formation of nanoalloys from mixtures of aqueous solutions of noble metal ions seems to follow similar patterns as elemental noble metals, i.e. it is governed by transfer of charge from ionized species, presumably ionized water species, to the metal ions, as proposed in the reduction reactions in the Supplementary Material and schematically depicted in figure 5. H₂PtCl₆ and HAuCl₄ are both strong acids and the dissociated anions, PtCl₆²⁻ and AuCl₄⁻ have been reported to readily react with water resulting in chloroaquahydroxo complexes of PtIV, [PtCl₄(H₂O)]⁻ (from NMR, in acidic conditions) and AuIII ions, [AuCl₄(OH)]⁻ (from Cl⁻ chromatography, also in acidic conditions). Similar hydrolysis reactions might be expected for PdCl₄²⁻. Until the reaction mechanisms are elucidated, we can, at this stage, only speculate that reaction of these complexes with ionized water species results in the simultaneous reduction of the metallic ions that lead to the final result observed in this work, schematically shown in figure 5. That variation of the molar ratio of the participating ions results in nanoalloys with corresponding compositions might somewhat consolidate this assumption.

Figure 3. SE micrograph and corresponding EDS analysis as well as elemental line scan profiles of a Pt-Pd-Au ternary alloy NP on a nanocarbon film. The carbon, oxygen and fluorine peaks belong to the substrate that consists of pyrolysed PVDF and CNT.
Considering table S1, it appears that the Pt content in the nanoalloys does not scale in a simple manner with the mixture ratios of the solutions. The alloys are always poorer in Pt than they should be according to the Pt content in the solutions. Admitting that the ions are reduced by ionized species, an explanation of the low Pt content might be suggested if we take into account the high potential of roughly 1.4 V (and therefore of the high charge) necessary for the reduction of PtCl$_6^{2-}$, in comparison to 1 V for AuCl$_4^-$ and 0.6 V for PdCl$_4^{2-}$. 

**Figure 4.** (a) Normalized and fitted XRD patterns in the range of the (111) peaks in grazing incidence mode. (b) Pd-, (c) and (d) Pt-concentration obtained using the corresponding 111 peak and Vegard’s law.

**Figure 5.** Schematic mechanism suggested for the metal ion reduction leading to the formation of an alloy.
3.4. Application to electrocatalysis

Catalytic applications of nanoalloys are manifold and range from CO oxidation to organic synthesis [5, 6, 30]. One of their most widely investigated properties relates to electrocatalysis, e.g. for fuel cell applications. We conducted appropriate experiments for methanol and formic acid electro-oxidation using our supported nanoalloys with the compositions Pt18Au82, Pd14Au86 and Pt52Pd48 as well as for the ternary alloy Pt51Pd22Au27.

3.4.1. Methanol electro-oxidation

The current-voltage (CV) loops in 0.5 M H2SO4 are displayed in figure S5 (Supplementary Material). While the hydrogen desorption peaks between 0 and 0.2 V are well visible, only weak humps can be seen in the range from 0.6 to 0.8 V that can be attributed to the reduction of Pt- and/or Pd-oxide which denotes the very small loading of the catalytically active NPs in our samples (e.g. compare our CV curves to those of Pozio et al [31] with well-known Pt-loading). This becomes even clearer when the methanol oxidation curves, figure S5, are displayed, underscoring the outstanding electrocatalytic performance of our nanoalloys.

Further, the electrocatalytic performance is controlled by the amount of the active element (Pd, Pt or both) on surface sites. We follow the electrochemical method devised in [23, 24] to determine the surface concentration of Pt and Pd of the alloys used in the electrocatalytic experiments (more details can also be found in the experimental section, 2.3). The values obtained, and listed in table 1, show that the surface of the alloys is enriched with Pt for Au-Pt and Pd for Au-Pd. Although the values certainly contain a non-negligible error margin, not least because the reduction peaks are very weak, they nonetheless suggest surface site enrichment with the active elements that is indirectly corroborated by the electrocatalytic results. Structural models of Au-Pt-NPs rather suggest Au-enrichment at the surface, leading to Pt-core-Au-shell NPs [32, 33]. These structural models may seem to be supported by surface segregation investigations of Au-Pt bulk alloys [34], but cannot explain the outstanding electrocatalytic activity of Au-Pt-alloy NPs reported in the literature [23, 35, 36]. More advanced studies based on modern analytical techniques, e.g. resonant high-energy XRD coupled with atomic pair distribution functions analysis and computer simulations [36] suggest that Au-Pt-NPs of different compositions rather consist of disordered fcc alloys, and that this structure is preserved even when the nanoparticles are annealed at 800 °C. The results obtained in the present work rather suggest, in agreement with the work of Petkov et al [36], the formation of metastable solid solutions the electrocatalytic behavior of which suggests Pt and Pd-surface enrichment. If we consider that the nanoalloy NPs form via direct reduction of the precursors then the formation of Au-Pt nanoalloys with Pt-rich surface might be explained by the higher reduction voltage of (PtCl6)2− against that of (AuCl4)− (see above and the Supplementary Material). But the results of the Au-Pd-nanoalloys are intriguing because in this case the reduction potential of (PdCl4)2−, 0.59 V is lower than that of (AuCl4)−, 1 V. At this stage we can only speculate that the formation of the nanoalloy NPs and their surface chemistry is not only governed by the reduction potential of the precursors but also by the kinetics of their reduction, possibly involving thermal decomposition effects on the substrate surface [37].

Figure 6 comparatively shows the mass activity, related to the Pt-content, of the nanoalloys for the electrocatalytic oxidation of methanol in aqueous acidic solutions. The corresponding CV-curves are shown in figure S6 (Supplementary Material). The peak current densities in figure 6(a) are displayed after subtracting the double layer charge contribution; their values are listed in table S2 (Supplementary Material) together with the on-set voltages. Apart from the Au-Pt-nanoalloy the performance of the other nanoalloys substantially exceeds that of Pt-NPs with the ternary nanoalloy performing best. Literature review suggests no conclusive results about the performance of Au-Pt nanoalloys in comparison to Pt, e.g. compare the results reported in references [36, 38–40]. To cite only two among them, Petkov et al [36] report for their best performing alloy, Au80Pt20, a mass activity (related to total metal mass, in acidic solution) that is very close to that of pure Pt, while Mott et al [40] show rather a very low activity of the same alloy under similar conditions. This discrepancy may originate from the surface chemistry of the nanoalloys that probably is contingent on the type of processing method employed. The present results on Pt-Au are similar to those reported in reference [41].

The Pd-Pt-nanoalloy shows a slightly higher mass activity than Pt. Similar results were obtained by Liu et al [42], particularly as to the relative difference between the nanoalloy and Pt (in their case BASF Pt), although their experimental conditions were different. But overall few results on this system are available in the literature, with one additional work that reports huge mass activity values approaching 1800 A g−1 for Pd16Pt84 [8].

The ternary Au-Pt-Pd nanoalloy shows the highest mass activity which peaks at 1244 A g−1 (forward peak) that is more than double the values of the other nanoalloys and monometallic Pt; it also affords the lowest on-set voltage which is of advantage because the reaction is triggered at lower cell voltages. Zhu et al [43] report ternary Au-Pt-Pd alloy nanowires (NW) processed in solution using sacrificial Te-NW; they also reported a higher electrocatalytic performance for their ternary alloys in comparison to the binary ones, although a direct comparison to the present work cannot be made, because they tested their alloys for ethanol electrooxidation in alkaline electrolytes. Guo et al [44] report on nanowires of FePtPd-alloys that were synthesized in solution using a combined thermal decomposition and reduction method [44]. Their results on the electrocatalytic oxidation
Table 1. Calculation of the surface composition using reduction peaks in the current-voltage loops in 0.5 M H₂SO₄ (figure S5) compared to alloy composition from the XRD (figure 4) or EDS analysis.

| Composition       | Pt surface composition in at. % | Pd surface composition in at. % | Au surface composition in at. % | Pt concentration in at.% obtained using Vegard’s law (or area EDS) | Pd concentration in at.% obtained using Vegard’s law (or area EDS) | Au concentration in at.% obtained using Vegard’s law (or area EDS) |
|-------------------|--------------------------------|--------------------------------|--------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| Pt₁₈Au₈₂          | 91.9                           | 0                              | 8.1                            | 18                                                              | 0                                                              | 82                                                              |
| Pt₁₄Au₈₆          | 0                              | 89.7                           | 10.3                           | 0                                                               | 14                                                              | 86                                                              |
| Pt₅₂Pd₄₈          | 61.4                           | 38.6                           | 0                              | 52                                                              | 48                                                              | 0                                                               |
| Pt₁₅Pd₂₂Au₂₇       | 10.6                           | 24.9                           | 64.5                           | (51)                                                            | (22)                                                            | (27)                                                            |
of methanol, though in HClO₄, show a moderate mass activity of approximately 450 A g⁻¹ that is approximately double the value of their PtPd-NPs. In a recent work, Wu et al [45] describe the performance of PtPd-3d transition metals alloys NPs for ORR, where the mass activity of various ternary alloys, particularly PtPdCu was correlated with the lattice constant after oxidative-reductive treatment cycles. It appears that a tuned NP composition of equal atomic fractions of Pt and Pd (Pt₂₀Pd₂₀Cu₆₀) with a compressed lattice results in the best catalytic performance and durability. In another report, trimetallic core-shell NPs, namely Au@Pd@Pt were processed using a co-reduction technique [46] where forward peaks of approximately 430 A g⁻¹ were obtained at similar experimental conditions, i.e. electrolyte and sweep voltage, to those of the present work. The authors ascribe their mass activity to the formation of a pseudo-Pt-Pd alloy at the surface of the NPs, meaning that electronic effects (ligand-effect) are responsible for superior electrocatalytic activity in comparison to Au@Pt and Pt NPs. This seems to coincide with the present results on the Pd-Pt nanoalloy, figure 6(a).

With regards to long-term stability and resistance to poisoning, the chronoamperograms displayed in figure 6(c) are additional proof of the substantially higher performance of the ternary nanoalloy in comparison to the Pt-NPs catalyst. The chronoamperograms were recorded at 0.8 V, below the peak voltages in forward sweep, of both the ternary nanoalloy and Pt-NPs, and should allow an appraisal of the resistance of the catalysts to site blocking species during the electrocatalytic reaction. It is obvious from figure 6(c) that, although the ternary alloy is also prone to poisoning, it nonetheless is characterized by a smoother descending slope as compared to Pt-NPs and the other nanoalloys. For instance, the activity decrease of the ternary nanoalloys is 66% after 1800 s, in comparison to 98% for the PtPd nanoalloy (for more detail see table S4 (Supplementary Material) which lists the activity decrease for the different NPs).

3.4.2. Formic acid electro-oxidation
Pt, Pd and their alloys as well as core-shells with other noble metals are powerful catalysts for formic acid (FA) electro-oxidation, although Pt is also prone to poisoning [47–49]. The mechanisms of FA electro-oxidation are still under discussion, particularly as to the nature of active adsorbed intermediates and site blocking species [49, 50], but there is a consensus on two different electro-oxidation pathways, namely the direct (direct hydrogenation of FA with the formation of CO₂ and H₂) and the indirect pathway (dehydration of FA with the formation of adsorbed CO), although mixed mechanisms do also operate, depending on material, voltage, temperature and pH [50].

Figure 6. (a) Current density (current normalized by the Pt-mass) versus voltage (Scan rate: 50 mV s⁻¹), (b) characteristic peak values obtained from (a), together with the peak voltages and (c) chronoamperograms (at 0.8 V versus NHE) with current densities versus time of the prepared sample electrodes in 0.5 M H₂SO₄ + 0.5 M CH₃OH. The full line curves correspond to Pt₀.₁₅Pd₀.₃₅Au₀.₅, the dashed dot line curves to Pt₀.₁₅Pd₀.₅Au₀.₃₅, the dashed dot-dot line curves to Pt₀.₁₅Au₀.₈₂, the short-dashed line curves to Pt-NPs modified electrodes.
The present results show specific behaviors of the systems investigated. Considering first the monometallic samples, figure 7(a) shows that Pt and Pd behave differently. In the case of Pt, there is first a hump centered at 0.55 V in the forward peak, followed by an intense peak at 0.95 V. The reverse sweep shows a strong hysteresis with a comparatively huge peak (about 4 times the intensity of the forward peak centered at 0.95 V) centered at 0.63 V. This behavior has been observed before and was ascribed to the main electrocatalytic mechanism being dominated by the indirect pathway (CO adsorption), with the existence of transient regimes \(^5\). With Pd, the electro-oxidation of FA starts at fairly low voltage, 0.2 V, peaks at 0.41 V and monotonically decreases for higher voltages up to 0.8 V where the activity is suppressed. On backward sweep, a slight hysteresis is observed with the onset of activity at approximately 0.8 V peaking at the same voltage as the forward sweep, with very similar peak intensity. This is a typical behavior of Pd surfaces where the activity is dominated by the direct pathway mechanism (adsorption of OH groups) \(^5\); what mostly distinguishes the present results from others is the extended range of activity from 0.2 to 0.8 V, in contrast to previous studies where the activity is steeply suppressed \(^5\). This behavior suggests that the Pd-NPs are more resistant to site blocking species. The Pd\(_{14}\)Au\(_{86}\) alloy shows a similar FA electro-oxidative behavior to Pd but with different peak positions and lower on-set voltages. A much more intense electrocatalytic activity can be seen in a wide voltage range between 0.1 and 1 V, with an intense peak at 0.38 V followed by a monotonous but steeper decrease of the activity in comparison to Pd. A shoulder appears at approximately 0.73 V after which the activity decreases at slightly lower rate and ceases
at approximately 1.1 versus On backward sweep, a moderate but broader hysteresis than Pd is observed with a steep increase in activity at 0.8 V followed by monotonous increase over a shoulder at 0.63 V towards the maximum that occurs at the same voltage as in the forward sweep. The results above demonstrate that with the AuPd nanoalloy the reactions are shifted to more negative voltage values than Pd, together with a substantially higher electrocatalytic activity. Because Au is not directly active in the electrocatalytic reaction, the following may be inferred: i) the Au-Pd alloy surface is probably enriched with randomly distributed Pd atoms or clusters in the Au matrix which is corroborated by the electrochemical results of table 1. Normally owing to the lower surface energy of Au Au segregation should be expected on a presumably Pd-enriched underlayer. But this is obviously not the case since the catalytic activity is rather boosted. This, once more, points to the metastable nature of the NPs processed under the present conditions; ii) Au indirectly participates in the electrocatalytic oxidation of FA either via inhibiting the formation of poisoning species on the surface of the Pd-atoms, e.g. by facilitating the oxidation of CO viz. the reaction between CO and OHad, or by weakening coverage with Hads. The latter may arise because Pd has a lower work function than Au which leads to a positive charge on Pd atoms neighboring Au (change in the local potential of zero charge). Consequently, catalytic site occupation by Hads should be hindered/minimized. Support of this mechanism may be seen in the CV curve (figure S7 (Supplementary Material)), where the electrocatalytic oxidation of FA already starts at the potential for hydrogen desorption.

A common feature of the Pt-containing alloys, i.e. Pt-Au, Pt-Pd and Au-Pt-Pd, is the similarity of their electrocatalytic behavior with that of monometallic Pt, as though Pt-sites constitute the main adsorption and catalytic sites. This is clearly illustrated in figure 7 with, however, few specific differences as to the intensity and loci of the peak maxima (compare figure 7(d) and table S3 (Supplementary Material)). The first peak between 0.2 and 0.8V corresponds to the first oxidation of FA. The peak maxima of the nanoalloys AuPt and AuPdPd are by at least one order of magnitude larger than Pt-NPs, but they are similar in their magnitude, with the ternary nanoalloy showing slightly higher peak voltages. At higher voltages there is a decrease in activity without, however, its complete suppression, and a second peak appears at a higher voltage that arises because the surface sites are regenerated by the oxidation of poisoning species, specifically adsorbed CO (e.g. by OHad). The backward peak that is significantly amplified with regards to the forward peak occurs at slightly different voltages ranging from 0.5 (Au-Pt Pd) to 0.6 V (for the ternary nanoalloy). This peak arises because adsorbed CO is oxidized into CO2, and results in the experiments in a considerable gas evolution. The behavior described above is common to Pt on which the electro-oxidation of FA is known to follow the indirect (hydration) mechanism. From the above it may be stated that, based on the common electrocatalytic behavior, the surface of Pt-containing nanoalloys is enriched with Pt, and this indirectly confirm the electrochemical findings depicted in table S3 (Supplementary Material). Nevertheless, the nanoalloys are substantially more active in the whole voltage range which, supposing a Pt-rich shell, could be explained by a shift in the density of state of the Pt surface atoms [53].

Considering the long-term behavior, it is intriguing that the nanoalloys AuPtPd and Pt-NPs perform better that the Pt-containing nanoalloys, although the electrooxidation mechanisms of the latter follow the direct path. At the indicated voltage there is over 90% decrease in activity of the Pd and Pd containing nanoalloys, whereas the activity AuPtPd and Pt decrease by approximately 75% (see table S4, Supplementary Material for more detail).

4. Conclusion

The present work demonstrated an easy and reproducible method to decorate large area nanocarbon surfaces with nanoalloy NPs of the system (Au, Pt, Pd). Both binary and ternary nanoalloys are processed from aqueous mixed ions solutions, and their composition can be tuned by varying the mixture ratio of the elements. In this method, a nanocarbon surface is preheated to a temperature slightly above the Leidenfrost-temperature and directly quenched in the mixture of the noble metal ions. The simultaneous reduction of the noble metal ions on the surface occurs without the need of a reducing agent, presumably by charge transfer from ionized species during the quenching process. A high density of homogeneously and well adherent alloy NPs is obtained in this manner, allowing only the surface to be modified, and is in this respect highly material efficient. The nanoalloy NPs can be advantageously applied for catalysis, and their overall high performance in the electrooxidation of methanol and formic acid in acidic solutions is demonstrated. Particularly the ternary nanoalloy shows the best properties in terms of methanol electrooxidation, although its Pt content is rather low. For formic acid electrooxidation Au-Pd-alloys show better properties as to the activity range and degree of hysteresis, although their long-term performance is rather poor. In contrast the Pt-containing nanoalloys, and particularly the ternary nanoalloy show better long-term properties.
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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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