# Symmetrical Pt(100) Nanoalloy Electrocatalysts for Ammonia Oxidation

## Stephen Nzioki Mailu*.

*Department of Physical Sciences, Machakos University, P.O Box 136-90100, Machakos, Kenya.*
*Corresponding author: Stephen Nzioki Mailu;*

*Abstract:*
*Novel Pt(100)Pd, Pt(100)Au and Pt(100)PdAu nanoalloys were synthesised and tested for ammonia oxidation, which is a structure sensitive reaction that occurs almost exclusively on Pt(100) sites. High resolution transmission electron microscopy (HRTEM) analysis showed well distributed non-agglomerated 5-20 nm semi-spherical and cubic nanoalloys with lattice fridges on their surfaces indicating the crystalline nature of the nanoalloys. The existence of the preferentially cubic shaped nanoalloys in the samples revealed that the nanoalloys had a significant amount of (100) sites at their surfaces. The cyclic voltammetry (CV) of the Pt(100) nanoparticles in the hydrogen adsorption/desorption region (-200 mV to 100 mV vs. Ag/AgCl) showed the presence of adsorption states associated with (110) sites, (100) domains and (100) sites at -131 mV, -34 mV and 29 mV, respectively. The absence of the peak observed at 29 mV in the Pt(100) nanoalloy systems confirmed the formation of the bimetallic and ternary nanoparticles. The electrochemical activity of these nanoparticles for ammonia oxidation in basic medium showed increased current densities compared to the Pt electrode.*
*Keywords: Nanoalloy, Nanoparticles, Catalyst, Ammonia oxidation, Adatoms*
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## I.  Introduction

The electrochemical oxidation of ammonia on transition metals and nanoparticles has been receiving considerable attention particularly in connection with its application in environmental electrocatalysis, electrochemical detection of ammonia and in electrochemical fuel cells [1]. Ammonia has attracted attention as a possible fuel for direct fuel cells since it is easy to handle and to transport as liquid or concentrated aqueous solution [2]. Its equilibrium potential is low;

$$N_{2(g)} + 6H^{+}_{(aq)} + 6e^{-} \Leftrightarrow 2NH_{3(aq)} \qquad\qquad E^{\theta} = -0.0092 \text{ V} \qquad\qquad (1)$$

and the theoretical charge for oxidation of $N_2$ is 4.75 $Ahg^{-1}$ that compares very well with the theoretical charge of methanol in its oxidation to $CO_2$ 5.02 $Ahg^{-1}$ [3]. However, ammonia electro-oxidation is a slow process at low temperature on noble metals and efficient catalysts are required to convert ammonia to nitrogen and hydrogen at reasonable reaction rates [3]. Several studies have been devoted to the development of efficient catalysts for ammonia oxidation. Various bimetallic catalysts have previously been investigated, e.g., Pt-Ir, Pt-Ir-Rh, Pt-Ru, Pt-Ni, Pt-Pd [4-9] and metal oxide electrodes, e.g., $IrO_2$, PtOx-IrOx and Ni/NiOx electrodes [10-14]. Most of these reactions were done using bulk metal or metal oxide electrodes with high precious metal loading. In order to develop efficient and economically viable electrodes, the amount of precious metals must be reduced. This can be achieved by using electrocatalysts in the form of nanoparticles which are considered as required materials for practical purposes [4]. It is noteworthy that majority of the electrocatalytic reactions are structure sensitive or site demanding such as $O_2$ reduction, $N_2H_4$ oxidation, $CO_2$ reduction and ammonia oxidation; thus controlling the crystallographic surface orientation of nanoparticles could result in much improved catalysts [15]. Ammonia on platinum surfaces occurs predominantly on Pt(100) sites [16]. Therefore, in order to develop good electro-catalysts for the ammonia oxidation, a major goal would be the preparation of nanoparticles with the largest density of Pt(100) sites. However, bimetallic and multi-metallic nanoparticles show higher catalytic properties than monometallic nanoparticles. This work demonstrates for the first time the catalytic effects that exist on Pt(100) nanoparticles upon the inclusion of adatoms such as Au, Pd and Pd-Au to form nanoalloys/nanocomposites for the ammonia oxidation reaction.

## II.  Experimental Methods
### 2.1 Synthesis of preferentially oriented Pt(100) nanoalloy systems

Pt(100)PdAu nanoalloys were synthesized as follows: 0.1 mL of a 0.1 M sodium polyacrylate solution was added to a 100 mL of an aged solution containing $1\times10^{-4}$ M $K_2PtCl_6$, $1\times10^{-4}$ M $PdCl_2$ and $1\times10^{-4}$ M

$HAuCl_4$. Argon gas was bubbled for 20 min followed by the reduction of metal ions using $H_2$ gas for 5 min. The reaction vessel was then sealed and the solution left overnight. After complete reduction (16 h) two NaOH pellets were added to the solution to produce a precipitate of the nanoparticles. After complete precipitation, the nanoparticles were washed 3–4 times with ultra-pure water. Pt(100), Pt(100)Pd, and Pt(100)Au nanoalloys were synthesized following the same procedure.

**2.2 Preparation of the electrodes and measurements.**

For the electrochemical characterization of the nanoparticles, 10 μL of the synthesized nanoparticles were drop-coated on the surface of Pt electrode and dried at room temperature. Electrochemical measurements were performed in a 0.5 M $H_2SO_4$ solution at room temperature. All voltammetric measurements were performed on a BAS 100W electrochemical workstation from BioAnalytical Systems Incorporation (Lafayette, USA) using a three-electrode system consisting of Pt electrode (1.6 mm diameter), Ag/AgCl (saturated NaCl) and platinum wire as working, reference and counter electrodes, respectively. All experimental solutions were purged with high purity argon gas and blanketed with the same during measurements. UV-visible spectra measurements were recorded with the Nicolette Evolution 100 Spectrometer (Thermo Electron Corporation, UK). High resolution transmission electron microscopy (HRTEM) images were acquired using a Tecnai $G^2$ $F_2O$ X-Twin MAT. For the catalytic oxidation of ammonia, the electrochemical measurements were performed at 25 ºC in 0.1 M ammonia and 1 M KOH aqueous solution saturated with argon gas.

## III. Result and Discussions

**3.1 Characterization of the nanoalloys**

**3.1.1 UV-visible spectroscopy**

The formation of the nanoparticles by reduction of $PtCl_6^{2-}$, $HAuCl_4^-$ and $Pd^{2+}$ ions was confirmed by the use of UV-visible spectroscopy. Fig. 1A shows the UV-visible spectra of the starting materials while Fig. 1B shows the UV-visible spectra of Pt(100), Pt(100)Pd, Pt(100)Au, Pt(100)PdAu nanoparticles. The absorption peaks observed at 262 nm for $K_2PtCl_6.3H_2O$ salt, 285 nm for $HAuCl_4.3H_2O$ and 420 nm for $PdCl_2$ salt (attributed to the existence of Pd(II)) [17-18] disappeared after 16 h of reduction indicating that the $[PtCl_6]^{2-}$, $HAuCl_4^-$ and $Pb^{2+}$ ions were completely reduced to zero-valent nanoparticles [19]. The colour of the solution turned from pale yellow to black.
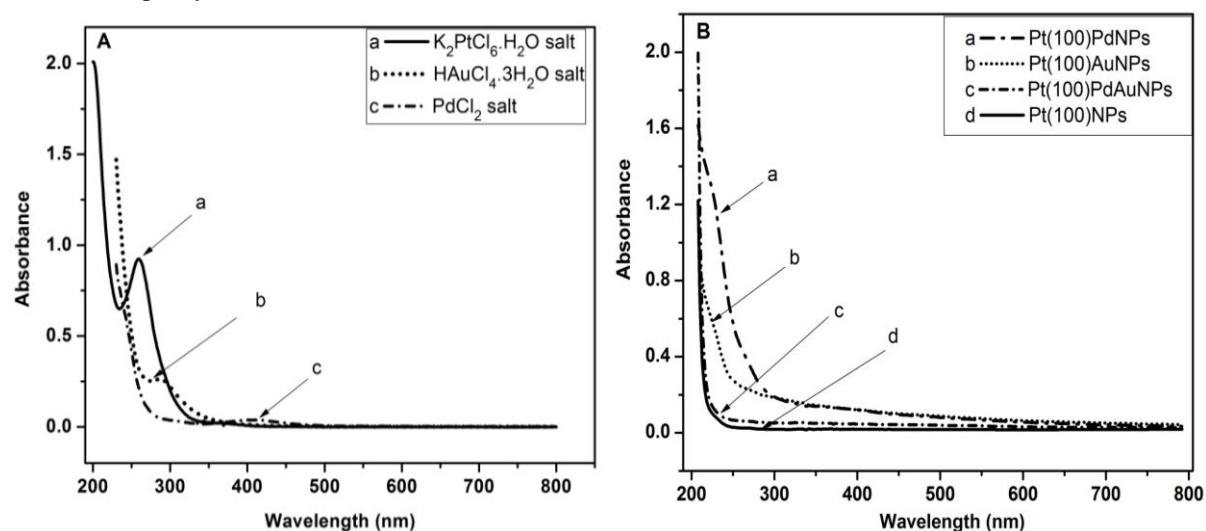


**Figure 1.** A) UV-vis spectra of $K_2PtCl_6.3H_2O$, $HAuCl_4.3H_2O$ and $PdCl_2$ salts and B) UV-vis spectra of Pt(100), Pt(100)Pd, Pt(100)Au and Pt(100)PdAu nanoparticles.

**3.1.2 High resolution transmission electron microscopy**

A very good characterization of the structure, shape and size of nanoparticles can be obtained by ex situ HRTEM. 5-10 nm sized Pt nanoparticles with a high amount of cubic shaped nanoparticles which is a characteristic feature of (100) oriented nanoparticles was observed (Fig. 2A) [17]. Pt(100)Pd nanoalloys (Fig. 2B) showed particles with triangular and cubic shapes while Pt(100)Au nanoalloys (Fig. 2C) and Pt(100)PdAu nanoalloys (Fig. 2D) showed well dispersed particles with some cubic shaped particles. The existence of the preferentially cubic shaped nanoparticles in the samples indicated that the nanoalloys had some (100) sites orientation/a significant amount of (100) sites at their surfaces. Well distributed nanoparticles throughout the samples were evident with no agglomeration observed and all the nanoparticles showed lattice fringes on their surface indicating that the particles were crystalline.
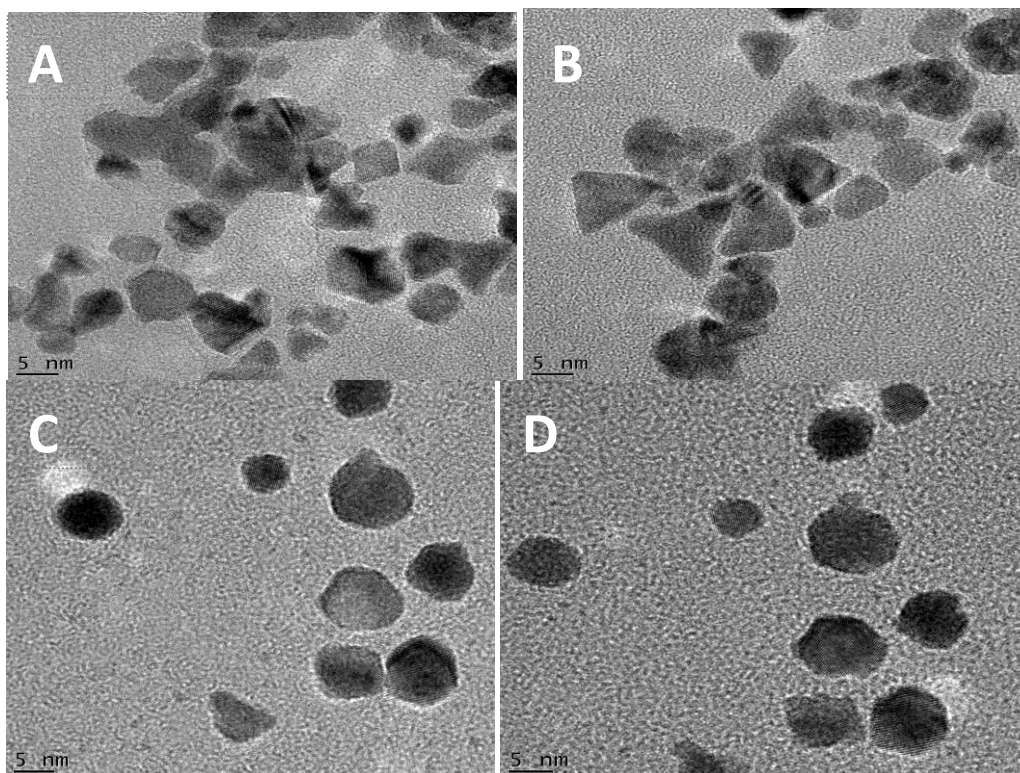
**Figure 2**. HRTEM images of Pt(100) nanoparticles (A), Pt(100)Pd nanoalloys (B), Pt(100)Au nanoalloys (C) and Pt(100)PdAu nanoalloys (D).

### 3.1.3 Electrochemical characterization

In order to characterize in situ the structure of the nanoparticles, cyclic voltammetry (CV) was used [17]. In the case of platinum, it is known that the so-called hydrogen adsorption/desorption process is very sensitive to the Pt surface structure [20] and this fact put in evidence is shown in the voltammetric profiles shown in Fig. 3. The voltammetric profiles work as a fingerprint for any Pt surface and from the voltammograms it is possible to obtain qualitative information of the nature and density of the surface sites. Fig. 3(A) shows the voltammogram of Pt(100) nanoparticles showing very clearly the presence of adsorption states associated with (110) sites (peak a/a') and (100) sites (peak b/b') at -131 mV and -33 mV, respectively. A redox peak at around 29 mV (peak c/c') was observed associated with (100) site [17, 21]. A poorly defined redox peak around 445 mV (peak d/d') was observed characteristic of small (111) ordered surface domains. It is noteworthy that the (111) domains are not well pronounced compared to the (100) sites indicating that the synthesized nanoparticles contained more of the (100) sites. The comparison of this voltammetric profile with that obtained for a Pt(100) single crystal electrode [22] clearly points out that the synthesized Pt nanoparticles have a higher density of Pt(100) sites. Fig. 3(B) shows a voltammogram characteristic of quasi-spherical Pt nanoparticles prepared in presence of sodium borohydride which looks similar to that reported for polycrystalline platinum electrodes [20].
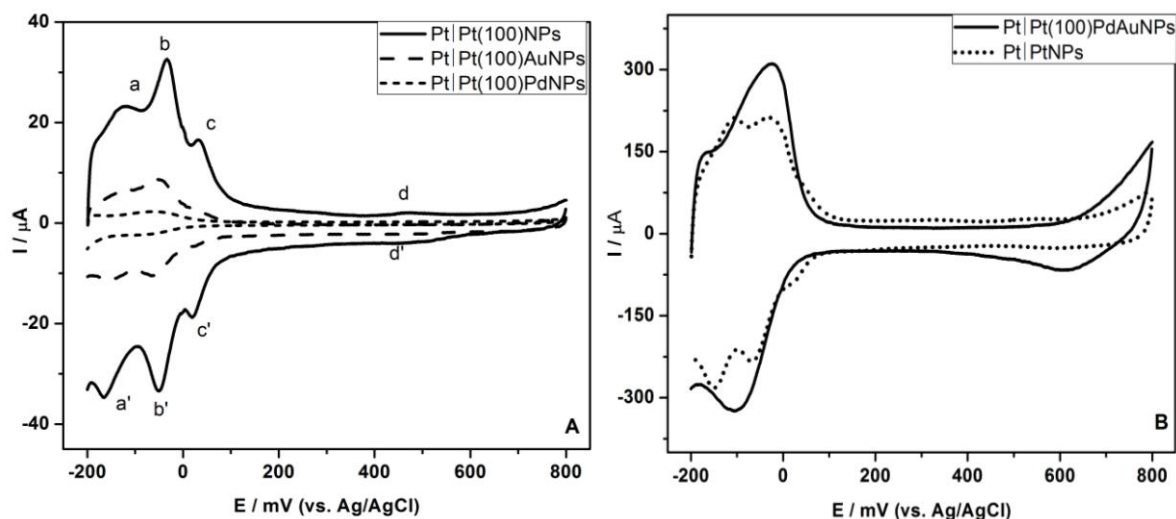
**Figure 3**. A) CVs of Pt|Pt(100)NPs, Pt|Pt(100)AuNPs and Pt|Pt(100)PdNPs and B) Pt|PtNPs and Pt|Pt(100)PdAuNPs in 0.5 M $H_2SO_4$, scan rate 20 mV s$^{-1}$

Pt(100)Pd nanoparticles (Fig. 3A) showed two peaks at 190 and -67 mV for the (110) and (100) sites. However, it can be observed that the Pd in the alloy blocked some of the (100) terraces indicated by the absence of the shoulder that is usually observed at 29 mV. Similar results were observe by Serrano-Ruiz [17] where the (100) terraces were blocked by Bi and Ge adatoms added to the oriented Pt(100) nanoparticles. However, Au was found to be moderately insensitive to the presence of Pt(100) surface sites (Fig. 3A). It is noteworthy that Pd-Au alloyed with Pt(100) was found to be sensitive to the Pt(100) sites and blocked some of the (100) terraces (Fig. 3B). The active surface areas (ESA) of Pt(100) nanoparticles and Pt(100) based nanoalloys were determined by the charge involved in the so-called hydrogen UPD region assuming 0.21 mC cm$^{-2}$ for the total charge after the subtraction of the double layer charging contribution [24]. ESA was estimated from the CVs according to the following equation [24]:

$$ESA = \frac{Q_H}{Q_H^O} \tag{2}$$

Where $Q_H$ is the charge for the hydrogen adsorption (mC) and $Q_H^O$ is the specific charge for a monolayer of hydrogen on Pt (0.21 mC cm$^{-2}$) [24]. ESA values of 0.01, 12.69, 8.86, 8.22, 7.42 cm$^2$ for polycrystalline Pt nanoparticles, Pt(100), Pt(100)Au, Pt(100)Pd and Pt(100)PdAu nanoparticles were obtained respectively. The results show that the Pt(100) nanoparticles have higher ESA than the nanoalloys. However, the nanoalloys/nanocomposites are known to portray better catalytic properties than the monometallic nanoparticles. This is worth interrogating with respect to ammonia oxidation reaction.

**3.1.4 Electrocatalytic oxidation of ammonia**

Fig. 4 shows the CVs of the oriented nanoparticles modified Pt electrode in 1 M KOH aqueous solutions in the presence of ammonia. The anodic current peak at -292 mV (Ag/AgCl) can be assigned to the oxidation of ammonia to $N_2$ while the anodic peak at about -930 mV is associated with the oxidation of hydrogen atom generated during cathodic process [25]. When the Pt electrode was coated with the nanoparticles, there was a current increase and lower overpotential compared to the bare electrode. Since the ammonia concentration was kept constant in all the experiments, the increased peak currents on the nanoparticles modified Pt electrodes may suggest that the active sites are denser than on bare Pt electrode. Although the Pt(100)Pd, Pt(100)Au and Pt(100)PdAu nanocomposites were expected to have a higher catalytic effect than the monometallic Pt(100) nanoparticles, the increased (100) sites in the monometallic system may have favoured the increased catalytic ammonia oxidation activity. Pt(100)PdAu nanoalloys had the lowest amount of Pt(100) sites and ESA thus gave the lowest oxidation current while Pt(100)Pd and Pt(100)Au nanoalloys showed a higher current due to the increased Pt(100) sites and ESA. A significant enhancement on the ammonia oxidation current was obtained when the preferential (100) colloidal Pt nanoparticles were employed. These voltammograms clearly points out that ammonia oxidation reaction is strongly influenced by the density of (100) sites on the nanoparticles and alloying Pt(100) with Pd and Au did not significantly improve the catalytic properties of Pt(100) nanoparticles. However, the oriented nanoalloys showed higher current densities than the polyoriented ones (e.g. those that contain Pt(100) combined with Pt(110): data not shown). Rh

and Ir have previously been shown to have high catalytic effects towards ammonia oxidation. Alloying them with Pt(100) nanoparticles and interrogating their catalytic effects forms the basis for our next research.
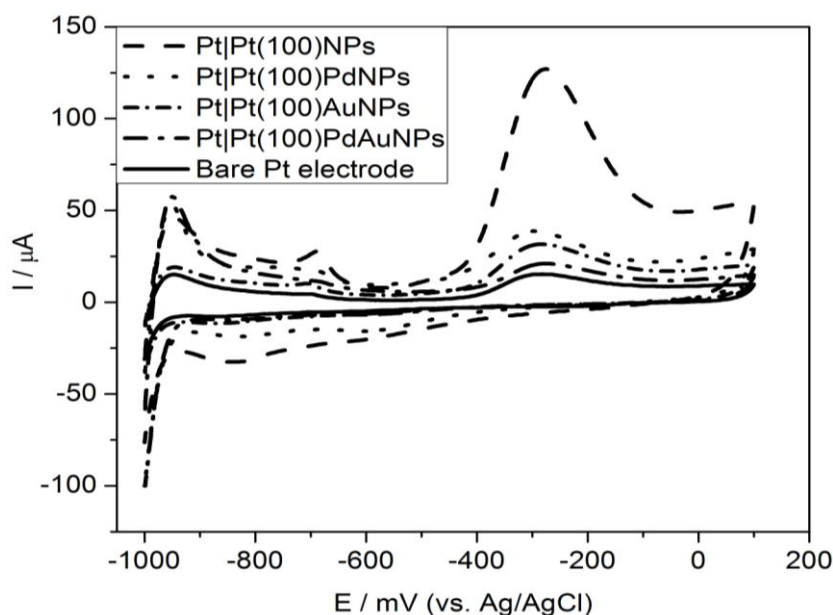


**Figure 4.** CV of Pt|Pt(100)NPs, Pt|Pt(100)PdNPs, Pt|Pt(100)AuNPs and Pt|Pt(100)PdAuNPs in 1 M KOH and 0.1 M ammonia. Scan rate 100 mV s$^{-1}$.

## IV. Conclusion

Pt based nanoalloys with (100) preferentially oriented surface structures were successfully synthesized and their activities for ammonia oxidation in basic medium were studied. The results show that ammonia oxidation is very sensitive to the existence of Pt(100) sites. Ammonia oxidation current for Pt(100) nanoparticles was higher than what was observed for bare Pt and Pt(100)Pd electrodes by factors of eight and six, respectively. Although these results indicate the importance of controlling the surface structure of the electrocatalysts for ammonia oxidation, other metals such as Rh and Ir alloyed with Pt(100) is worth investigating.

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