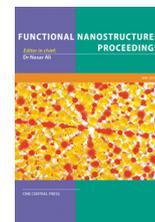


Available online at [www.onecentralpress.com](http://www.onecentralpress.com)

One Central Press

proceedings webpage: [www.onecentralpress.com/functional-nanostructures-proceedings](http://www.onecentralpress.com/functional-nanostructures-proceedings)

# Fabrication of $\text{CoIr}_x/\gamma\text{-Al}_2\text{O}_3$ modified electrode and use in electrochemical oxidation of hydrazine

Naveeda Firdous<sup>1</sup>, Naveed KausarJanjua<sup>2\*</sup>

<sup>1,2</sup>Department of Chemistry, Quaid-i-Azam University, Islamabad-45320, Pakistan.

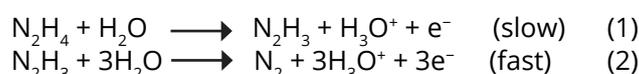
\*corresponding author

## KEYWORDS

Co-Ir nanoalloys supported on  $\gamma\text{-Al}_2\text{O}_3$ ; bimetallic catalysts; hydrazine electro-oxidation; cyclic voltammetry; electrocatalysis.

## I. INTRODUCTION

Hydrazine is considered as supreme source for direct fuel cell, as no carbon atom is present in the structure, thus leading to Co-free products [1]. The use of hydrazine ( $\text{N}_2\text{H}_4$ ) in the present world is inevitable, although it is hazardous however ( $\text{N}_2\text{H}_4$ ) is an ideal liquid for direct liquid-feed fuel cells. Hydrazine and its derivatives are basically used in industry, agriculture, and other fields including fabrication of metal films, photographic compounds, explosives, insecticides and blowing agents for plastics [2]. Latest investigations have revealed adverse effect of hydrazine on health. Hence, an efficient setup is needed to monitor sensitive detection of hydrazine, in ecological and biotic analysis. In this respect, various methods had been reported such as, spectrophotometric, spectrophotometric flow injection, liquid chromatography, gas chromatography-mass spectrometry, titrimetry, coulometry, amperometry, potentiometry, and voltammetry [3-7]. Electrochemical practices provide a prospect for portable, cost-effective, sensitive, and speedy methodologies. In this context, a great focus has been made on the design and development of novel electrocatalysts for hydrazine oxidation and detection [8]. For electrocatalytic performance, metal nanoparticles are more advantageous due to high surface area, good durability, high dispersion, controlled particle size, morphology, chemical inertness, good electrical and mechanical properties [9-12]. The oxidation mechanism of hydrazine can be described by Eqs. 1 and 2. The rate determining step involved one-electron transfer followed by a three-electron transfer to give  $\text{N}_2$  as a final product.



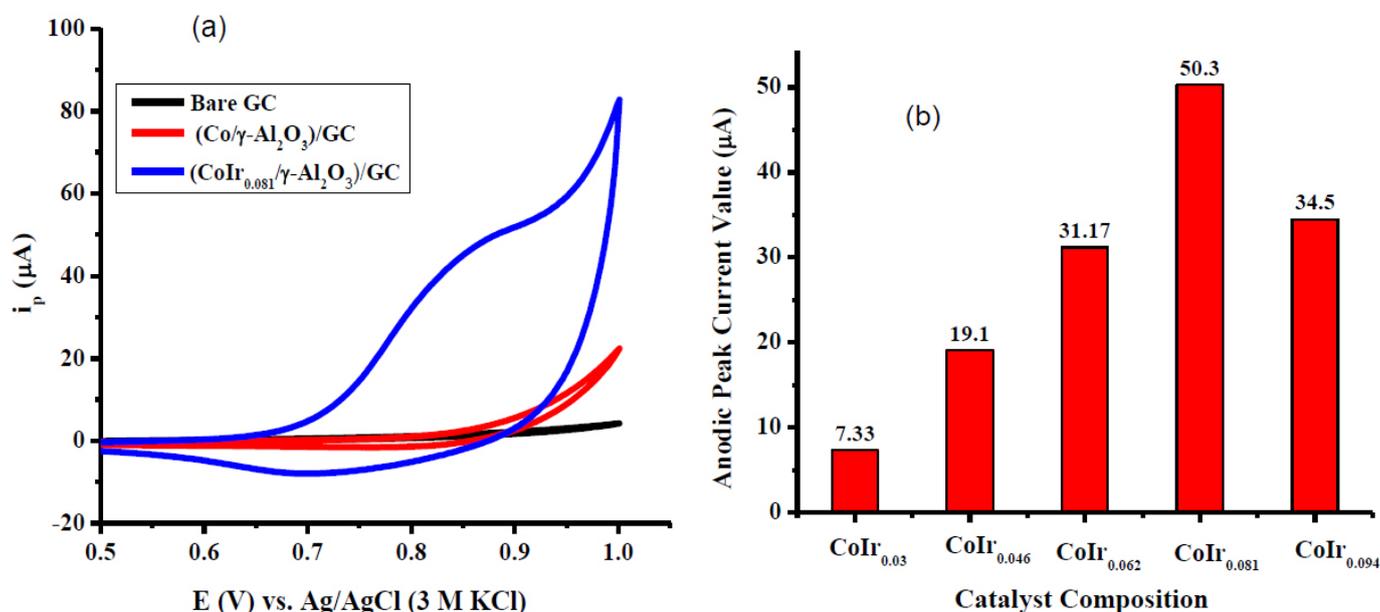
## II. EXPERIMENTAL

In the present work, a series of bimetallic catalyst  $\text{CoIr}_x/\gamma\text{-Al}_2\text{O}_3$  ( $x$ , Ir mole ratio= 0, 0.03, 0.046, 0.062, 0.081 and 0.094) was synthesized via wet impregnation method as described earlier [13]. The desired metal contents in  $\text{CoIr}_x/\gamma\text{-Al}_2\text{O}_3$  catalyst series were achieved in multi-step impregnations followed by  $\text{H}_2$  reduction

at 550 °C for 4 h. The prepared catalysts were characterized by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron spectroscopy (TEM), energy dispersive X-ray spectroscopy (EDX), Surface area analysis (BET method), temperature programmed reduction and oxidation (TPR/TPO) analysis which ensure the elemental composition, crystal structure, morphology, surface properties and synergistic effect between two metals to form Co-Ir alloy nanoparticles.

### III. RESULTS AND DISCUSSION

Electrocatalytic oxidation of hydrazine was investigated on  $\text{CoIr}_x/\gamma\text{-Al}_2\text{O}_3$  modified glassy carbon electrode (GCE) using cyclic voltammetry technique. Hydrazine electroactivity was tested in KOH by using  $\text{CoIr}_x/\gamma\text{-Al}_2\text{O}_3$  modified GCE. 0.1 mg of very fine catalyst powder was dispersed in 5  $\mu\text{L}$  ethanol. The modification was done by introducing 2  $\mu\text{L}$  of catalyst/ethanol dispersion on a clean surface of GC followed by drop casting of 2  $\mu\text{L}$  Nafion (0.5%) solution and dried. All catalysts gave the electrochemical response for hydrazine electro-oxidation. Fig. 1a shows that bare GC electrode presented no anodic peak current while; poor current response for monometallic  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  modified GCE without any oxidation peak for hydrazine. Due to the addition of Ir metal, it greatly reduced the overpotential for the hydrazine oxidation in comparison to pure Co which might be due to the alloying effect of Co and Ir in addition to better metal dispersion and high surface area.  $\text{CoIr}_{0.081}/\gamma\text{-Al}_2\text{O}_3$  was selected as an optimal composition in the series because of its prominent electrocatalytic response with peak current value of 50  $\mu\text{A}$  at 0.88 V. The comparison of catalysts within series is shown in Fig. 1b as bar graph. The present data also indicated that this set of materials can contribute towards further applications in the field of electroanalysis.



**Figure 1** (a) Cyclic voltammograms of  $\text{CoIr}_{0.08}/\gamma\text{-Al}_2\text{O}_3$  modified electrodes for 2mM hydrazine electro-oxidation in 0.1 M PBS (pH 7.2) @ 25  $\text{mV s}^{-1}$ . (b) The comparison for the performance of  $\text{CoIr}_x/\gamma\text{-Al}_2\text{O}_3$  catalysts towards hydrazine electro-oxidation.

The effect of scan rate on oxidation peak current was also examined in the range of 10-100  $\text{mV s}^{-1}$  for  $\text{CoIr}_{0.081}/\gamma\text{-Al}_2\text{O}_3$  modified electrode. With increasing scan rate, the anodic peak potential was noticed to shift slightly towards more positive region suggesting a kinetic limitation in the reaction between the modified electrode and hydrazine. The anodic peak current was found to increase linearly with the square root of scan rate, suggesting that the overall electro-oxidation process at this electrode is governed by diffusion of hydrazine to the redox sites of the modified electrode. The effect of hydrazine concentration was also studied on  $\text{CoIr}_{0.081}/\gamma\text{-Al}_2\text{O}_3$  in the range of 2-10 mM in 0.1 M phosphate buffer solution, PBS (pH 7.2). The anodic peak current at the modified electrode was found proportional to the hydrazine concentration.

### IV. CONCLUSIONS

On the basis of electrochemical results,  $\text{CoIr}_{0.081}/\gamma\text{-Al}_2\text{O}_3$  is proposed as a promising candidate for extensive electroanalytical applications prospects. In conclusion, the optimal loading of Co and Ir onto  $\gamma\text{-Al}_2\text{O}_3$  support has proven as an effective composition. The present study also indicated that this set of materials can contribute towards further applications in the field of electroanalysis and hydrazine sensing in analytical application.

---

**V. REFERENCES**

- [1] M. Zheng, Y. Zhou, Y. Chen, Y. Tang, T. Lu, Electrochemical behavior of dopamine in the presence of phosphonate and the determination of dopamine at phosphonate modified zirconia films electrode with highly antifouling capability, *Electrochimica Acta*, 55 (2010) 4789-4798.
- [2] A. Umar, M. Rahman, Y.-B. Hahn, Ultra-sensitive hydrazine chemical sensor based on high-aspect-ratio ZnO nanowires, *Talanta*, 77 (2009) 1376-1380.
- [3] M. George, K. Nagaraja, N. Balasubramanian, Spectrophotometric determination of hydrazine, *Talanta*, 75 (2008) 27-31.
- [4] M. Mori, K. Tanaka, Q. Xu, M. Ikedo, H. Taoda, W. Hu, Highly sensitive determination of hydrazine ion by ion-exclusion chromatography with ion-exchange enhancement of conductivity detection, *Journal of Chromatography A*, 1039 (2004) 135-139.
- [5] M. Michlmayr, D. T. Sawyer, Electrochemical oxidation of hydrazine and of the dimethylhydrazines in dimethylsulfoxide at a platinum electrode, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 23 (1969) 375-385.
- [6] W. Hou, H. Ji, E. Wang, Amperometric flow-injection analysis of hydrazine by electrocatalytic oxidation at cobalt tetraphenylporphyrin modified electrode with heat treatment, *Talanta*, 39 (1992) 45-50.
- [7] S. Chakraborty, C. R. Raj, Carbon nanotube supported platinum nanoparticles for the voltammetric sensing of hydrazine, *Sensors and Actuators B: Chemical*, 147 (2010) 222-227.
- [8] A. A. Ensafi, E. Mirmomtaz, Electrocatalytic oxidation of hydrazine with pyrogallol red as a mediator on glassy carbon electrode, *Journal of Electroanalytical Chemistry*, 583 (2005) 176-183.
- [9] C. M. Welch, R. G. Compton, The use of nanoparticles in electroanalysis: a review, *Analytical and Bioanalytical Chemistry*, 384 (2006) 601-619.
- [10] L. Shaidarova, G. Budnikov, Chemically modified electrodes based on noble metals, polymer films, or their composites in organic voltammetry, *Journal of Analytical Chemistry*, 63 (2008) 922.
- [11] M. Oyama, Recent nanoarchitectures in metal nanoparticle-modified electrodes for electroanalysis, *Analytical Sciences*, 26 (2010) 1-12.
- [12] B. Dong, B.-L. He, J. Huang, G.-Y. Gao, Z. Yang, H.-L. Li, High dispersion and electrocatalytic activity of Pd/titanium dioxide nanotubes catalysts for hydrazine oxidation, *Journal of Power Sources*, 175 (2008) 266-271.
- [13] N. Firdous, N. K. Janjua, I. Qazi, M. H. S. Wattoo, Optimal Co-Ir bimetallic catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for hydrogen generation from hydrous hydrazine, *International Journal of Hydrogen Energy*, 41 (2016) 984-995.
- [14] A. Benvidi, P. Kakoolaki, H. R. Zare, R. Vafazadeh, Electrocatalytic oxidation of hydrazine at a Co(II) complex multi-wall carbon nanotube modified carbon paste electrode, *Electrochimica Acta*, 56 (2011) 2045-2050.