



## Cu-Pd Bimetallic Catalyst for Electrocatalytic Reduction of Nitrates in Water

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**Abstract:** This paper reports the use of bimetallic catalysts, prepared via co-electrodeposition of Cu and Pd from chloride baths in 0.5 M HNO<sub>3</sub> on Ti substrates and its catalytic effect on nitrate reduction. Electrochemical measurements were made using cyclic and linear sweep voltammetry while deposition was made via chronopotentiometry at -0.5 V vs Ag/AgCl. Scanning electron microscopy analyses revealed that the films produced by potentiostatic deposition are porous and rough, which is suitable for electrocatalysis applications. Results show that prepared electrocatalyst was able to reduce nitrates with 86.50% efficiency after 3 hours. Meanwhile, soaking the electrocatalyst in tap water over time decreases its efficiency to some extent but still capable of reducing high concentration of nitrates in water.

**Keywords:** potentiostatic electrodeposition; bimetallic catalyst; electrochemical reduction; nitrates

### 1. Introduction

Many rivers, lakes and ground waters are continuously being contaminated with nitrates from misused fertilizers and industrial wastes. This poses an important problem not only for human health but also for the ecosystems. When inside the human body, nitrates can be reduced to nitrites that combine with hemoglobin to form methemoglobin, which can be deadly to newborn babies [1]. The need to regulate or remove such ions has stimulated intensive research from reduction techniques to reaction mechanisms. Methods used for nitrate reduction are classified under physico-chemical, biological and electrochemical [2]. Examples are biological denitrification and ion exchange. But these methods have known drawbacks like the need for continuous monitoring, slow kinetics and by-product formation [2]. Recently, researchers have given more focus on electrochemical methods due to good efficiency, low cost and lesser reagents. Reducing the nitrate ion is one of the few ways to regulate or remove such pollutants from water and electrochemical reduction of nitrates gives a relatively broad spectrum of products. This tells us that the mechanism behind the reduction is not easy. However, many ways were developed to optimize the parameters behind the process. The catalytic reduction with hydrogen was one of the first methods to garner attention [3]. Monometallic catalysts were also used but bimetallic catalysts were found to be more efficient in heterogeneous catalytic reduction of nitrates [4, 5]. The catalyst is usually composed of a noble metal, mainly Pd or Pt but also Ru, Rh or Ir, and a promoter metal, such as Cu, Sn, Ag, Ni, In or Fe, on different supports like alumina, silica and activated carbon [6]. Among them, Pd-Cu, Pd-Sn and Pt-Cu seem to be more effective but lack selectivity to nitrogen [7]. Moreover, the method of preparation, the metal/promoter ratio, the operation conditions and the interaction between metals control the catalyst's activity and selectivity [8]. For the past years, copper-palladium alloys have gained the spotlight due to their widespread potential use in many electrocatalytic applications. Many papers have been published dealing with various techniques for the deposition of bimetallic/alloy copper-palladium coatings like sputtering, chemical vapor deposition and pulsed- laser techniques [9, 10]. But these methods were limited for laboratory investigations and not into large scale production. On the other hand, electroless plating and electrodeposition are two preparation methods that offer good results for small and large scale productions. While a number of researches have been done in this area, but very few have been published on co-electrodeposition of Cu-Pd alloys. Notably, Reyter *et al.* [2] and Milhano and Pletcher [11] were able to co-electrodeposit Cu-Pd alloys over a wide range of composition from nitrate-based and sulfate-based baths respectively.

This study presents Cu-Pd alloys prepared via co-electrodeposition using chloride-based baths. Potentiostatic electrodeposition was carried out and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDXS) were used to characterize the Cu-Pd deposits. Then, the effect of the prepared electrocatalyst was investigated on nitrate reduction efficiency.



## 2. Experimental

### 2.1 Materials

All aqueous solutions prepared in this study were made with distilled water from AquaMax Ultra (Yonglin Instruments Inc.; resistivity 18.2 MΩ\*cm). The deposition solution bath was made consisting of 8 mM/ 5 mM CuCl<sub>2</sub> and PdCl<sub>2</sub> with 0.5 M HNO<sub>3</sub>. Synthetic nitrate solutions with initial concentration of 100 mg/L were prepared using KNO<sub>3</sub> (Oriental Chemical Industries, Korea) in distilled water. Most chemicals were purchased from Sigma Aldrich Corporation or otherwise mentioned.

### 2.2 Preparation of Electrocatalyst and Electrochemical Measurements

All electrodeposition experiments were done at room temperature in a three-electrode, one compartment cell with a potentiostat/galvanostat Autolab Eco Chemie PGSTAT100. A platinum electrode and saturated Ag/AgCl electrode were used as counter and reference electrode respectively. Thus, all potentials reported in this study are referenced to its potential. 1 M or 2 M NaOH solution was used as the supporting electrolyte. Titanium foil, with a surface area of 1x1 cm<sup>2</sup>, was used as substrates for the deposition. Electrodes were first polished with abrasive paper then cleaned in hot (80° C) 1 M HCl solution and then wash with distilled water. Again the electrodes were agitated in acetone using an ultrasonic bath for 15 min and finally rinse with distilled water. Electrodeposition was made using chronopotentiometry method at -0.5 V for 300 s from a deposition solution consisting of 0.5 M HNO<sub>3</sub> in the presence of (i) 10 mM Pd(NO<sub>3</sub>)<sub>2</sub>, (ii) 10 mM Cu(NO<sub>3</sub>)<sub>2</sub>, and (iii) 10 mM Pd(NO<sub>3</sub>)<sub>2</sub> + 10 mM Cu(NO<sub>3</sub>)<sub>2</sub>

### 2.3 Characterization of the Prepared Electrocatalyst

The surface morphology of the electrodeposits and their compositions were examined using a field emission scanning electron microscope (FE-SEM, model HITACHI S-4800) at an accelerating voltage of 20 kV and energy dispersive X-ray spectroscopy (EDXS, model EX-250 Horiba) directly attached to the FE-SEM.

### 2.4 Reduction of Nitrates in Water

Approximately 5 mL of the prepared nitrate solution is poured into the electrochemical cell after which electrochemical measurements were made using linear sweep voltammetry from 0 to -1.5 V. At different time intervals, a 1 mL sample was drawn from the electrochemical cell for analysis. Nitrate concentration was then analyzed using a UV-VIS (MECASYS UV-Vis Spectrophotometer) colorimetric method at 410 nm utilizing the rapid determination of nitrate-N by complexation [12]. Moreover, the prepared electrocatalysts were also soaked in tap water for almost 10 weeks to test the stability of its activity towards nitrate reduction over time. Thus, every week the electrode's efficiency in reducing nitrates were tested as well.

## 3. Results and Discussions

### 3.1 Nitrate reduction experiment

Reported in Figure 1 are the linear potential scans for the (a) Ti-Pd, (b) Ti-Cu and (c) Ti-Cu/Pd electrodes in 2 M NaOH + 30 mM NaNO<sub>3</sub>. It can be seen that nitrate was not reduced on the palladium surface because the sharp reduction peak at around -0.10 V is not indicative of nitrate reduction but rather of hydrogen absorption on its surface or an oxidation/reduction of palladium. In contrast, nitrate reduction occurs to some extent on the Ti-Cu/Pd surface and two peaked cathodic waves are observed at 0.30 V and 0.13 V against Ag/AgCl. Similar-formed cathodic waves were discussed by Milhano *et al* [11] but the shifting of the peak might be the different metal used as substrate. The two peaks may be linked to the different forms of nitrogen ions produce in the reaction but it is also worthy to note that we cannot directly attribute the two waves to reactions leading to specific products. The Ti-Cu electrode demonstrated one cathodic peak at around 0.23 V against Ag/AgCl. Although reduction of nitrate was not observed on the Ti-Pd electrode, it complemented the Cu to cause a synergistic effect for efficient nitrate reduction.

The catalytic efficiency of nitrate reduction in higher nitrate concentrations was also tested with the Ti-Cu/Pd electrodes in a less basic medium. Figure 2 shows the voltammogram of the Ti-Cu/Pd electrode in just the NaCl supporting electrolyte alone, in dashed-lines and with additional 100 ppm nitrate solution in straight-line. As observed, reduction current increased in both blank and with NO<sub>3</sub><sup>-</sup> solution when the potential was lower than -0.4 V versus Ag/AgCl. This could be a result of the electrolysis of water into hydrogen, which was the main process observed. However, the reduction peak at around -0.65 V and -0.4 V indicates the characteristic reduction of nitrate in this medium (see straight-line) [13]

The catalytic nitrate reduction efficiency of the Ti-Cu/Pd, Ti-Cu and Ti-Pd electrodes were also tested. Table 1 shows the result of the test including just the bare substrate. From the results, co-electrodeposited alloy of Ti-Cu/Pd electrode demonstrated effectiveness towards nitrate reduction to lesser forms among the other



tested electrodes, with a reduction percentage of 70.4. This result proves that alloying of Cu with Pd remarkably improves the electrocatalytic activity of the electrode towards nitrate reduction. This also confirms with other previous studies [2]. Figure 3 depicts the effect of catalysis time of the electrodes on nitrate reduction. Increasing catalysis time leads to a corresponding decrease in nitrate concentration in solution mainly due to charge transfer-limited process. In a non-flow cell, the reaction is practically dependent on time. This shows that enough time is needed to transfer the ions to the cathode surface to completely reduce the nitrate to other forms. Therefore, catalysis time is also an important parameter to be considered when reducing nitrate ions concentration in water.

### 3.3 Characterization of Deposits

Figure 4 shows the SEM images of the different electrodes obtained by co-electrodeposition and the EDX showing the chemical composition of the films. The Cu/Pd films (a) presented a porous and cauliflower-like structure. The morphologies of (b) pure Pd (dendritic deposits) and (c) pure Cu (large crystals) films are very different from each other and from that of the Cu/Pd alloy films. Also, as seen in these images most electrodeposited coatings completely covered the Ti foil substrates. As mentioned, the Cu/Pd deposits produced cauliflower-like structures that are dome in shape and are amorphous. Moreover, alloying of Cu and Pd reduces the mean crystallite size and thus induces the formation of nanoscale structures, which can be of good value for electrocatalysis and surface applications [10]. While the Cu/Pd alloy film has porous, dome-like structure, the pure Cu film looks rougher crystals and that of the pure Pd are like dendrites. These results are in congruent with the results by the team of Allemand *et al* [10]. Figure 4 a, b and c corresponds to the EDX profiles of the Cu/Pd, pure Pd and pure Cu deposits, prepared by co-electrodeposition respectively. From the profiles, peaks corresponding to Ti are well pronounced compared to other metals in all cases. This may be attributed to the thin nature of the film deposited on the substrate with the giving concentrations. Table 2 shows the atomic composition of the Cu/Pd, pure Cu and pure Pd films. As mentioned earlier, higher Ti content is linked to the substrate, the Cu/Pd electrode had less percentage of Ti compared to the electrodes with pure Cu or pure Pd. Both EDX and SEM analyses demonstrate that Cu/Pd alloys can be deposited potentiostatically on Ti substrates over various composition ranges.

### 3.4 Effect of Soaking

The electrodes stability towards nitrate reduction was tested by soaking the electrodes in tap water and then used every week for nitrate reduction. Figure 5 shows the summary of the results of the tests after the 10<sup>th</sup> week. As expected, the better electrode was the Ti-Cu/Pd with averages of 63.29%, 79.67% and 86.50% after the first, second and third hours respectively of catalysis. Figure 6 reveals the SEM images of the electrodes after 10-weeks of soaking with 1-3 hour catalysis after every week. It should be noted that the surface of the cathode, where the metal cations are deposited, changes in properties over time especially when soaked in tap water, which has other cations (hardness) ions that affect the capacity of the electrocatalyst. In relation to this, additional control process may be required. However, the general features of the surface remained the same just like that shown in Figure 6 (a). Table 2 summarizes the surface composition of the electrocatalysts tested before and after soaking as analyzed using EDX. The elemental compositions of the Ti-Cu/Pd surface before and after soaking are  $\text{Cu}_{0.33}\text{Pd}_{0.14}$  and  $\text{Cu}_{0.17}\text{Pd}_{0.07}$  respectively. This shows that prolong use may cause some of the catalyst to fall off the substrate or be affected by other ions in solution and affect the ability of the electrocatalyst. Shown in Table 3 are the average percent efficiencies of the three kinds of electrodes used in this study. From the table, it can be concluded the Ti-Cu/Pd electrode demonstrated outstanding performance after 3 hours with a percentage efficiency of 86.50 compared to the other electrodes.

## 4. Conclusions

In this study Cu/Pd alloy films which were potentiostatic co-electrodeposited on Ti foil using  $\text{CuCl}_2$  and  $\text{PdCl}_2$  in 0.5 M  $\text{HNO}_3$  showed promising results for nitrate reduction in water. As seen in the SEM images, Cu/Pd films prepared in the potentiostatic mode were rough, porous and dome-like structures and were suitable for electrocatalysis applications. Although Ti-Pd electrode showed no activity toward nitrate reduction, it complemented the Cu in the Ti-Cu/Pd electrode to create the needed effect towards nitrate reduction. Furthermore, the prepared electrocatalysts showed superior stability in reducing nitrate ions even after being soaked in tap water for 10 weeks.

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#### Table titles

Table 1 Percent efficiencies of the different electrodes after 1 hour of catalysis at 0 to -1.5 V

Table 2 Surface composition of electrocatalysts before and after soaking test with catalysis at the end of the every week

Table 3 Average Percent Efficiencies of Electrodes after Soaking for 10 weeks

#### Figure captions

Figure 1 The linear potential scans for the (a) Pd film , (b) Cu film and (c) Cu-Pd film in 2 M NaOH + 30 mM NaNO<sub>3</sub>.

Figure 2 CV curve at 10 mV/s of the Ti-Cu/Pd in 0.5 g/L NaCl only (dashed line) and in 0.5 g/L NaCl + 100 ppm NO<sub>3</sub><sup>-</sup> solution (straight line).

Figure 3 Plot of nitrate concentration (absorbance) against catalysis time (hours).

Figure 4 shows the SEM images of the (a) Ti-Cu/Pd (b) Ti-Cu and (c) Ti-Pd obtained by co-electrodeposition and the EDX showing the corresponding chemical composition of the (a) Ti-Cu/Pd (b) Ti-Cu and (c) Ti-Pd.

Figure 5 Summary plot of the effectiveness of the electrodes after soaking in tap water for 10 weeks; (a) 1-hour catalysis, (b) 2-hour catalysis and (c) 3-hour catalysis.

Figure 6 SEM images of (a) Ti-Cu/Pd (b) Ti-Cu and (c) after 10-weeks of soaking with 1-3 hour catalysis after every week

#### Table 1



Catalyst (in 0.5 M HNO <sub>3</sub> )	NO <sub>3</sub> <sup>-</sup> concentration after catalysis/ppm	% Efficiency
Bare Ti	80.827	19.2 %
Ti-Cu	40.137	59.9 %
Ti-Pd	58.873	41.1 %
Ti-Cu/Pd	29.563	70.4 %

**Table 2**

Electrocatalyst (before/after soaking)	Atomic %			Elemental composition
	Ti %	Cu%	Pd%	
Ti-Cu/Pd before	64.15	20.99	14.86	Cu <sub>0.33</sub> Pd <sub>0.14</sub>
Ti-Cu/Pd after	48.87	10.89	7.52	Cu <sub>0.17</sub> Pd <sub>0.07</sub>
Ti-Cu before	88.38	11.62	-	Cu <sub>0.18</sub>
Ti-Cu after	35.21	2.90	-	Cu <sub>0.05</sub>
Ti-Pd before	83.18	-	16.82	Pd <sub>0.16</sub>
Ti-Pd after	70.67	-	10.88	Pd <sub>0.09</sub>

**Table 3**

Catalysis Time (hours)	Average nitrate reduction efficiency (%)		
	Ti-Cu/Pd	Ti-Cu	Ti-Pd
1	63.29	55.84	33.73
2	79.57	66.75	39.72
3	86.50	72.50	42.00

**Figure 1**

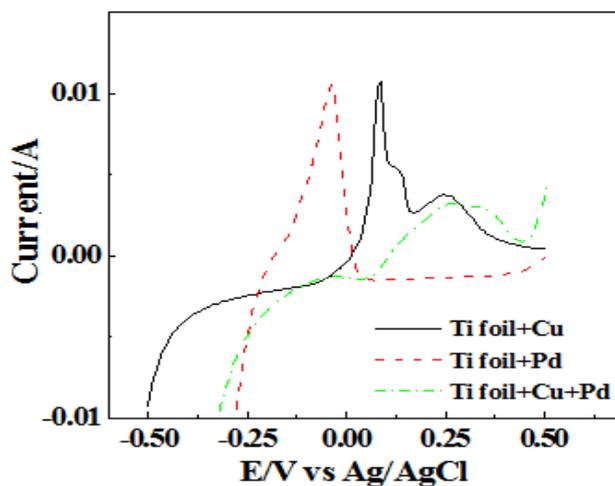


Figure 2

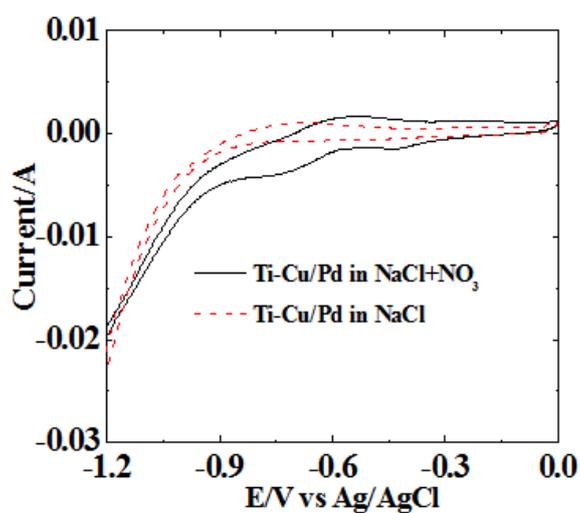


Figure 3

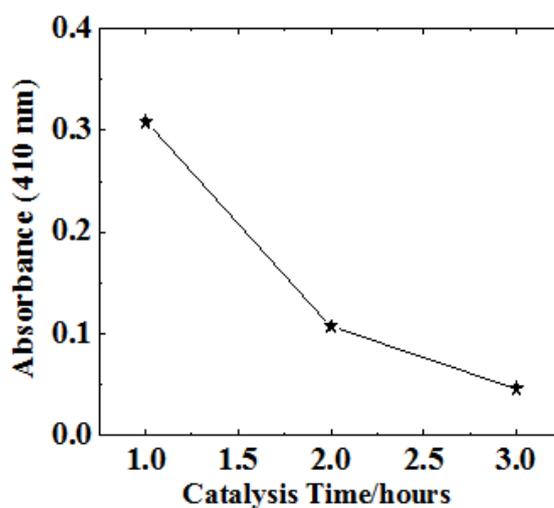


Figure 4

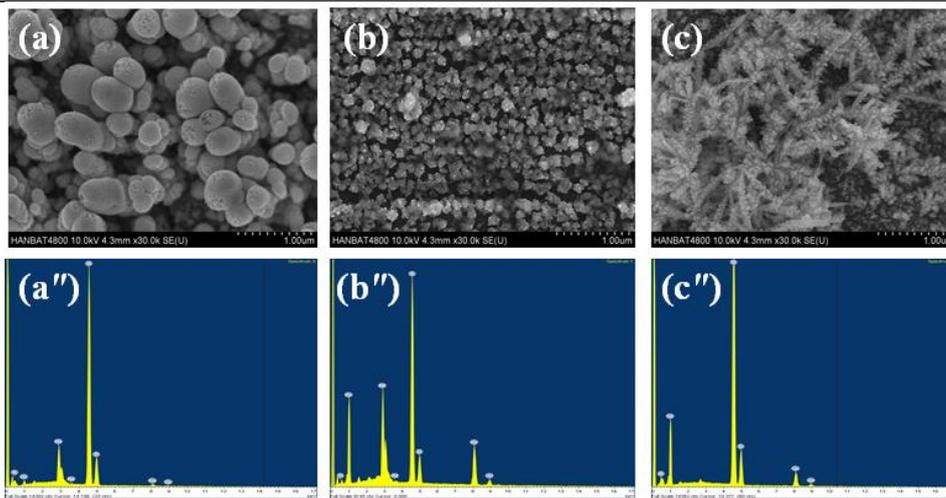


Figure 5

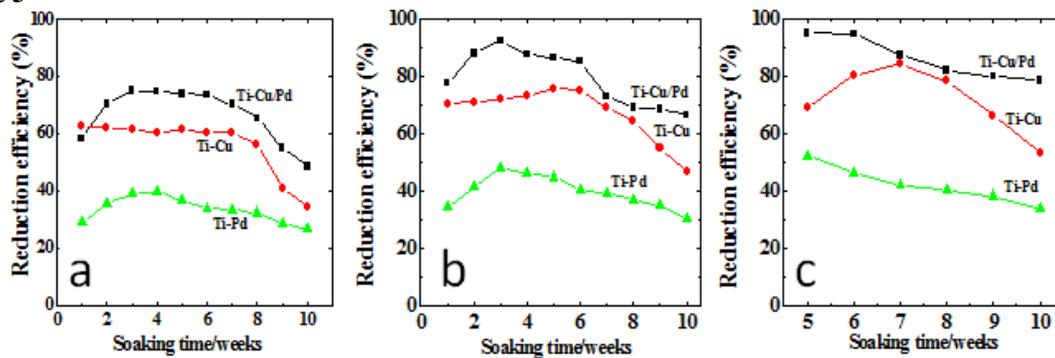


Figure 6

