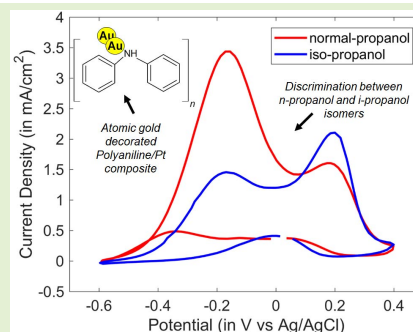


Design and Development of Amperometric Gas Sensor With Atomic Au–Polyaniline/Pt Composite

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Abstract—Rapid advancements in information processing and embedded systems require high selective and fast sensors. Conventional gas sensors are not suitable for the detection of isomers of organic compounds due to cross-sensitivity and the response time being limited by slow chemical kinetics. Amperometric gas sensors using conducting polymers modified with metal catalysts are a suitable and robust system due to many tunable properties. In this paper, conducting polymer polyaniline was electrochemically decorated with clusters containing precisely defined number of gold atoms to function as an electro-catalyst. The modified polymer composite showed fast reaction rate for the electro-oxidation of alcohols in both liquid and gas phases. The number of gold atoms affected the catalytic activity. Cyclic voltammograms were measured and results showed discriminable patterns between n-propanol and iso-propanol even at different gas concentrations. Thus, it was demonstrated that gas sensor arrays can be realized by decorating different number of gold atoms on polyaniline electrodes, to yield defined and different selectivity.

Index Terms—Amperometric gas sensor, atomic gold, conducting polymer, electro-catalyst, polyaniline, propanol.



I. INTRODUCTION

GAS sensors have a wide range of modern applications such as their use in breath analysis to detect anomaly in

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a patient's health, as security devices for monitoring gas leaks, quality control in the food industry etc. [1]. Conventional gas sensors, however, are known to face some common challenges such as cross-sensitivity to humidity [2] and amperometric gas sensors are electrochemical type of gas sensors that are a more robust choice due to their several merits [3] in terms of characteristics such as low power, ease of fabrication, and the ability to perform in humid conditions. Although such sensor characteristics are attractive, they come at a cost of slow chemical kinetics when operating at room temperature, and sensor microfabrication is often a complicated process [4]. In the past, our group studied a halitosis sensor based on an electrochemical sensor array [5], however, more work needs to be done to improve the selectivity, chemical kinetics and sensitivity of that sensor as well. In late 20th century, nanomaterials such as conducting polymers [6] became a popular choice for sensors due to their electrical conductivity, tunable properties and operation at room temperatures. One such conducting polymer is polyaniline (PANI) which has been popular due to its availability in several oxidation states, and which offers a wide range of tunable properties [7], [8].

In 1980, Diaz *et al.* demonstrated the synthesis of electroactive PANI films on electrodes by the electro-oxidation of aniline on a platinum (Pt) electrode in an acidic medium [9]. Since then, there have been several studies of polyaniline based

gas sensors such as using single-walled carbon nanotubes and nanocomposites [10]. Although such sensors show good sensor characteristics such as reproducibility and low detection limit, there is cross-sensitivity across similar chemical species. Furthermore, it becomes even more difficult for these sensors to classify structural isomers of organic compounds.

Since structural isomers have same molecular formula, we need to find suitable new materials that show different reaction response to such isomeric compounds. One such material is propanol that exists in two isomers viz. n-propanol (nPrOH) and iso-propanol (iPrOH). While iPrOH is a common solvent of choice in the printing industry and as a potential fuel for direct alcohol fuel cells (DAFCs), nPrOH is a major constituent in many kinds of cosmetics. In the past, metal oxide based propanol gas sensors with its detection levels of few tens of ppm in air have been reported [11]–[13]. Since they are susceptible to sensor drift and require high temperature operation for higher sensitivity, they are not suitable for discrimination between isomeric compounds at room temperature. While in the past, research has been conducted to discriminate between some isomeric compounds such as xylene [14], no sensors to discriminate between nPrOH and iPrOH have been reported. In 1987, Haruta *et al.* [15] introduced the use of gold (Au) as a catalyst for the oxidation of carbon monoxide. Later, Hatchett *et al.* [16] further demonstrated that the growth of Au clusters on PANI substrate by oxidizing the PANI and forming a metal halide complex. The small size of Au showed interesting properties and in the later years, the size of Au cluster was further reduced to atomic size. PANI doped with atomic Au showed enhanced electrocatalytic properties to electrooxidation of alcohols [17]. By controlling the oxidation potential of PANI, atom-by-atom cluster of gold could be deposited on PANI [18]. It has also been shown that depending on the number of Au atoms, the current response also shows an odd-even pattern due to the HOMO-LUMO energy gap of the Au clusters [19]. Such properties are important in the fabrication of novel gas sensor arrays [20], [21].

In this paper, the method of decoration of atomic Au on a conducting polymer to fabricate selective materials for gas sensors is reported. Although PANI doped with atomic Au has been used in the liquid phase, this is the first paper of its gas sensing behavior. Then, it was applied to the classification of nPrOH and iPrOH. Voltammograms of nPrOH and iPrOH at various gaseous concentrations showed discriminable patterns that were later classified using principal component analysis.

II. NOVEL SENSING MATERIALS

A. Method of Atomic Gold Deposition

It has been found that clusters of gold with precisely defined number of metal atoms exhibit unique electrocatalytic properties for oxidation of aliphatic alcohols [14]–[16]. In this paper we demonstrate how such materials could be used for construction of sensing arrays and multivariate chemical sensing analysis. The general concept of preparation of such materials is described in the following section.

Growing atom-by-atom gold clusters onto PANI is a cyclic process [18]. PANI inside an acidic medium can be oxidized to its imine form, which has the ability to form strong metal

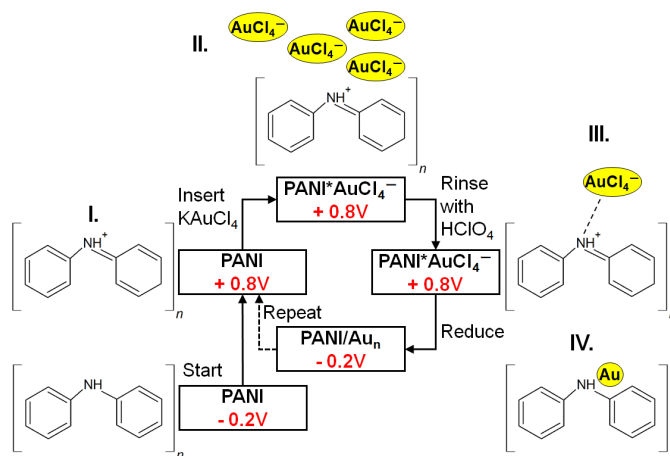


Fig. 1. Cyclic process of atomic gold deposition (I) PANI is oxidized by elevating the potential from -0.2 V to $+0.8$ V (II) Potential is held at $+0.8$ V. AuCl_4^- ions are introduced *in situ* (III) One of the AuCl_4^- ions forms a $\text{PANI}^*\text{AuCl}_4^-$ metal halide complex and excess AuCl_4^- is rinsed with HClO_4 buffer solution (IV) Potential is swept from $+0.8$ V to -0.2 V leading to the reduction of AuCl_4^- to Au. Atomic Au is decorated onto PANI. The process from I-IV can be repeated ‘N’ times for decorating ‘N’ atoms of Au (reproduced from [17]).

complex with halo-anions. According to Fig. 1, a Pt working electrode is first polymerized with PANI and the potential is swept from -0.2 V to $+0.8$ V at which PANI changes from its emeraldine form to electrophilic pernigraniline form (I). If a metal halide (e.g. tetrachloroaurate anion AuCl_4^-) is introduced *in situ*, then $\text{PANI}^*\text{AuCl}_4^-$ complex is formed due to the high electron affinity of PANI functional group in this state (II). Excess AuCl_4^- ions are rinsed out by acid buffer solution (III). By linearly sweeping the potential back to -0.2 V, Au^{3+} in AuCl_4^- is reduced to atomic Au^0 (IV). Since only a single AuCl_4^- anion is needed for each atomic Au deposition, the deposition can be performed at very low concentrations of AuCl_4^- . The cyclic process (I-IV) can be repeated ‘N’ times to grow ‘N’ atomic gold cluster onto PANI substrate, e.g. Au_2 means two gold atoms.

B. Catalytic Activity of Different Gold Depositions

Atomic Au has an effect on the electrocatalytic ability of PANI as experimentally demonstrated by Jonke *et al.* and gold clusters made up of 2 and 6 atoms have shown to possess the largest HOMO-LUMO gap and dissociation energy [19]. They also reported the FTIR spectroscopy of N-H stretching measured in the region of $3100\text{--}3500$ cm^{-1} in 0.1 M HClO_4 . The dependency of N-H stretching could be seen in the odd-even pattern obtained from the band areas relative to the number of atoms in the cluster. Since the thus formed Au atoms were expected to be close to the nitrogen sites of PANI, the magnitude of N-H stretching vibration therefore depended on the size and stability of those atomic Au clusters in PANI. In this research, the ‘odd-even pattern’ of PANI/Au_N composites was experimentally examined by first preparing atomic Au onto PANI and step-wise growing bigger clusters through a cyclic pathway to form different PANI/Au_N composites ($N = 0, 1, 2, 3$ and 4). After the preparation of composites, cyclic voltammogram scans were measured with

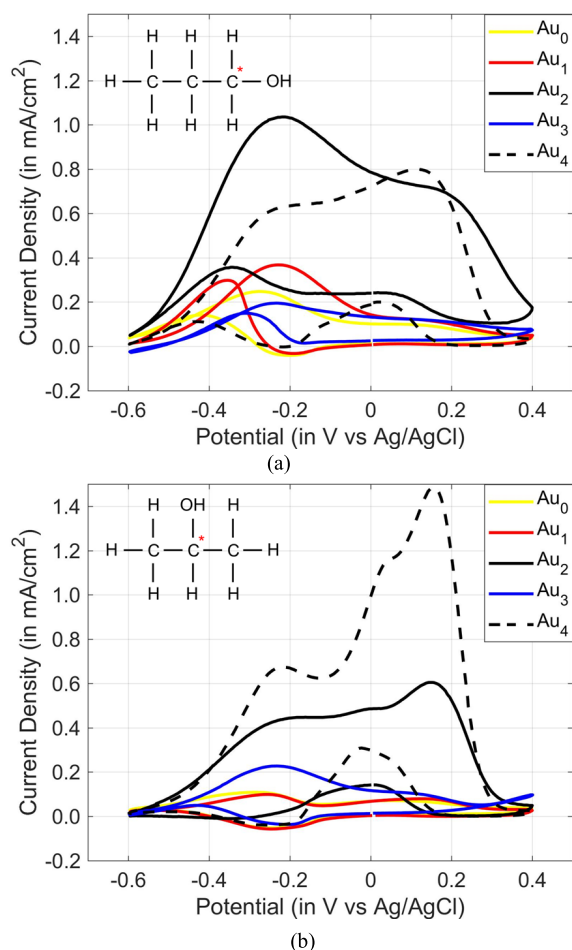


Fig. 2. CV of PANI/Au_N (N is the number of atomic gold decorated onto PANI; N = 0, 1, 2, 3 and 4) in (a) normal-propanol or nPrOH & (b) iso-propanol or iPrOH. Voltammograms show an odd-even pattern due to the variation in the HOMO-LUMO gap energy of atomic gold cluster (Scan Rate: 100 mV/sec).

each composite to perform the electrooxidation i.e. 0.5 M nPrOH and 0.5 M iPrOH in 1M KOH alkaline medium.

Two current density peaks were observed due to the oxidation of nPrOH and iPrOH to their intermediates providing evidence for selectivity. For electro catalytic oxidation of alcohols on gold, the rate-determining step is the cleavage of the C–H bond on the alcohol, which leads to the formation of alkoxide ion. For primary alcohol (e.g. nPrOH) the alkoxide is more active towards the electrochemical oxidation leading to propionic aldehyde, which can be further oxidized, while for the secondary alcohols (e.g. iPrOH) the final product is the corresponding ketone (e.g. acetone) [22]. Composites with odd number of gold atoms showed lower current density, whereas composites with even number of gold atoms showed a larger current density (Figs. 2 (a) and (b)). An additional oxidation peak at + 0.2 V was also seen for composites with even number of gold atoms. Furthermore, discriminable patterns were obtained between nPrOH and iPrOH. Due to the distinct change in the shape of CV and large current density of PANI/Au₂ composite, highly selective sensors are expected for both gas classification [23] and gas mixture quantification [5].

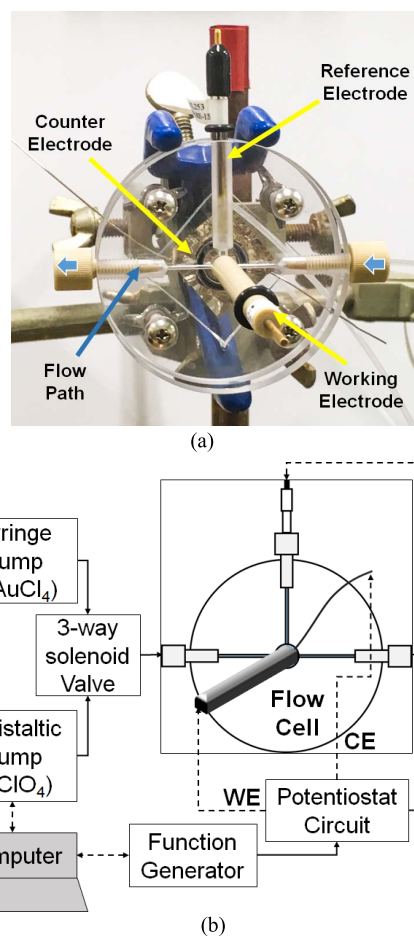


Fig. 3. Experimental setup (a) Flow cell for & (b) Atomic gold deposition system. (WE: Au decorated PANI/Pt working electrode, RE: Ag/AgCl reference electrode, CE: Pt thin film counter electrode connected with Pt wire).

III. MATERIALS AND METHODS

A. Experimental Setup for Atomic Au Cluster Insertion

Since the atomic gold deposition required parameters such as potential and electrolyte exposure time to be precisely controlled, a special polycarbonate flow cell (diameter $\varnothing = 60$ mm, Fig. 3 (a)), fabricated by Ono denki, Japan was used. Ag/AgCl in 3 M NaCl (BAS, Japan) and Pt thin film (Nilaco, Japan) were used as reference electrode (RE) and counter electrode (CE) respectively. The flow cell consisted of two plates – a front plate and a back plate. The Pt thin film CE was sealed between the two plates of the flow cell using an O-ring and polydimethylsiloxane (PDMS) membrane. Pt film created an exposure surface for the incoming electrolyte. PDMS was used as an elastic membrane to seal the two plates to prevent electrolyte leakage. Plastic washers were used negate the thrust created when hinging the two plates of the flow cell together.

0.2 mM potassium tetrachloroaurate (KAuCl₄) dissolved in 0.1 M perchloric acid (HClO₄) was used as gold solution for the insertion of gold atoms. 0.1 M HClO₄ was used as a buffer solution for rinsing excess gold ions. After the oxidation of PANI, a syringe pump (Legato 110, KD Scientific) was used to drive KAuCl₄ solution into the flow cell. HClO₄ was then used to rinse excess AuCl₄⁻ anions in the system and its injection was driven by a peristaltic pump (13-876-2, Fisher Scientific).

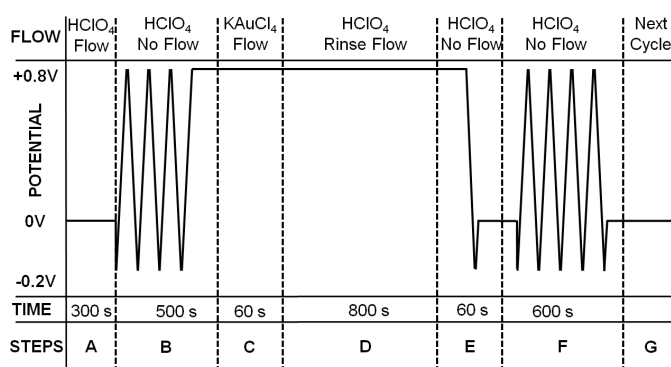


Fig. 4. Timing Diagram of flow cell for atomic gold deposition process. Y-AXIS shows the change in the working electrode potential while X-AXIS shows the time taken for each process to complete. FLOW indicates the different aqueous solutions entering the flow cell at each process. Steps 'A', 'B' are a pretreatment process of rinsing with HClO₄ buffer solution and scanning the CV of PANI before atomic gold deposition. At 'C', KAuCl₄ is introduced and at 'D'. RINSE FLOW indicates the use of the aqueous solution for rinsing the flow cell. In this case, HClO₄ buffer solution is used to rinse away excess AuCl₄⁻ ions for a period of 800 seconds. NO FLOW indicates no further flow of the respective aqueous solution into the flow cell. At this stage, the electrolyte inside the flow cell is kept constant. 'E' is the reduction of Au³⁺ to Au⁰ followed by 'F' which is the cleaning the PANI/Au_N composite by taking several CV scans. From 'G', the entire process can be repeated for higher atomic gold decorations.

A solenoid valve (EXAK-3, Takasago) was used to control the switching between solutions. Flow connections between apparatus were established using chemically inert tygon tubes (LMT-55, Saint Gobain) (Fig. 3 (b)).

The working electrode potential was controlled by a laboratory-fabricated potentiostat. A low-noise JFET operational amplifier (TL074, Texas Instruments) was used in the design of the potentiostat. Along with the potentiostat circuit, an Arduino was used to control the solenoid valves and the peristaltic pump. All devices were controlled and all measurements were taken using a Serial-USB protocol inside a MATLAB script file (2017a, Mathworks).

B. Preparation of Polyaniline (PANI)

PANI was prepared on a platinum Pt working electrode or WE (diameter $\varnothing = 3$ mm, BAS Japan) by electropolymerization of 0.1 M aniline (C₆H₅NH₂) in 2 M tetrafluoroboric acid (HBF₄) at constant potential using a three-electrode electrochemical setup. Total polymerization time was for about 200 seconds at a total charge transfer limit of 13 mC.

C. Timing Diagram of Flow Control for Au Cluster Insertion

The flow cell was first rinsed with 0.1 M HClO₄ buffer solution for 300 sec before inserting the PANI electrode into the flow cell (see timing diagram in Fig. 4). This step ensured that there were no air bubbles in the flow cell path. After rinsing the flow cell, the PANI electrode was inserted and potential was swept between -0.2 V and $+0.8$ V for three CV scan cycles at a scan rate of 20 mV/sec. This step was crucial for cleaning the surface of PANI.

Following this step, the potential was held at $+0.8$ V to maintain PANI in its oxidized imine state. 2 ml of 10^{-4} M KAuCl₄ was injected into the flow cell for an exposure time of 60 sec. At this stage, PANI formed PANI \cdot AuCl₄⁻ metal complex surrounded by excess AuCl₄⁻ anions. In order to remove the excess AuCl₄⁻ anions, the previous step was followed by rinsing with HClO₄ buffer solution for a period of about 800 sec. After the long rinsing stage, the potential was pulled down to -0.2 V leading to the reduction of Au³⁺ to Au⁰. The Au atom formed a coordinate bond with the nitrogen of PANI leading to the deposition of atomic size gold or Au₁. Following this, three CV scan cycles were taken to clean the PANI/Pt electrode decorated with Au₁. The process was repeated one more time to decorate PANI/Pt electrode with another atomic Au leading to the formation of PANI/Au₂ composite.

D. Gas Delivery System

In order to measure the CV response in gaseous phase, a gas delivery system was fabricated (Fig 5). The design is similar to an odorant delivery system [23], with an output channel flow rate of 200 ml/min. 1 ml of propanol sample was inserted into the vial to create an odor headspace and the gas was bubbled into a temperature controlled electrochemical cell. Two solenoid valves worked complementarily with each other and the concentration of the blended odor was controlled by switching the duty cycle of the solenoids. The gas delivery system was calibrated with a photoionization detector (ppbRAE 3000, RAE Systems) and vapors of nPrOH and iPrOH were generated at 30%, 60 and 90% of full-scale concentration of 1600 ppm of pure alcohol in air.

IV. RESULTS

Changes in the CV of PANI at each step of atomic gold deposition are discussed. Characteristics of PANI/Au₂ composite and its CV response to propanol in liquid phase and gas phase are reported. In case of multiple CV cycles, the last cycle of CV is plotted unless mentioned otherwise.

A. Cyclic Voltammetry of Atomic Au Deposition

In Fig. 6, the dotted line or curve I shows the initial CV scan of PANI in 0.1 M HClO₄. Curve II shows the first reduction of Au³⁺ to Au⁰. Curve III shows subsequent change in the CV shape. Similarly, curve IV shows the second Au³⁺ reduction and curve V shows the final CV scan. At the end of curve V, PANI/Au₂ composite is ready to be used for sensing experiments. From curves I-V, the backward scan shows an upward negative shift to the negative potential with each atomic gold decoration. This is due to the oxidative degradation of PANI when being held for a prolonged time at $+0.8$ V [18].

B. CV Response to Propanol in Liquid Phase

PANI/Au₂ composite was used to study the electrooxidation of propanols. Scan rate for all measurements was 100 mV/sec unless otherwise stated. Results showed that there was

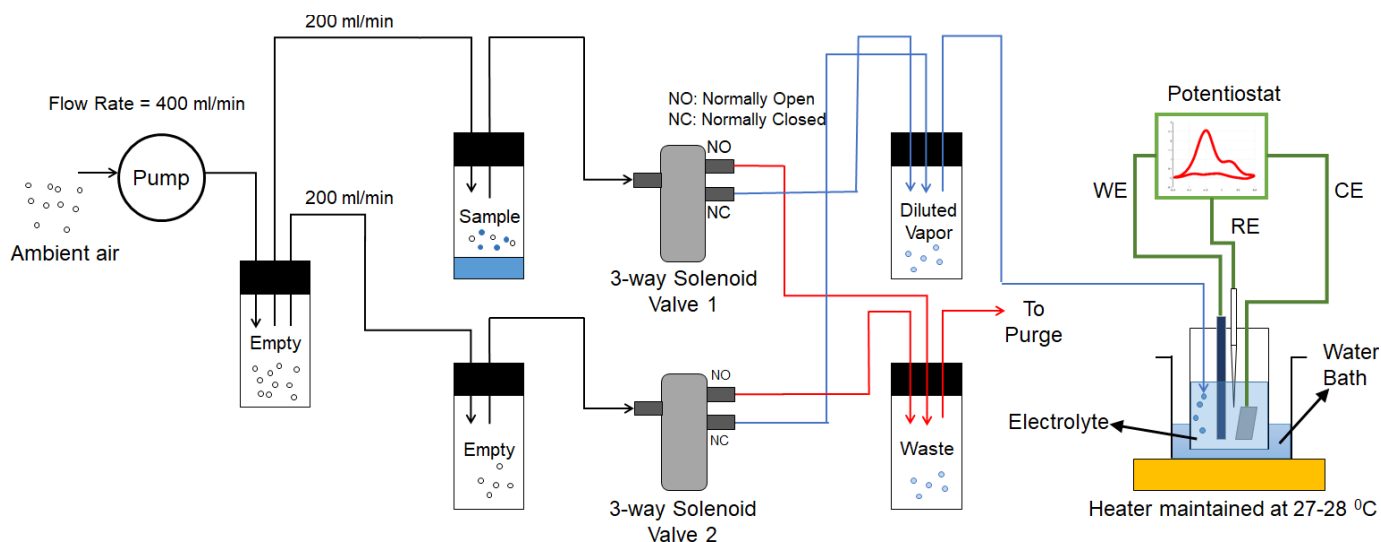


Fig. 5. Odorant delivery system and measurement system for CV in gaseous phase: Ambient air is pumped into an empty vial followed by two vials – one containing sample and the other one empty. Solenoid valves are used to create a ‘blended vapor’ by switching alternately at 1 Hz. By modifying the duty cycle, different concentrations are produced. The output for nPrOH and iPrOH sample at full-scale (100 %) concentration calibrated with photoionization detector was 1600 ppm. The blended vapor was bubbled into a 3-electrode electrochemical cell and the CV was measured using a potentiostat.

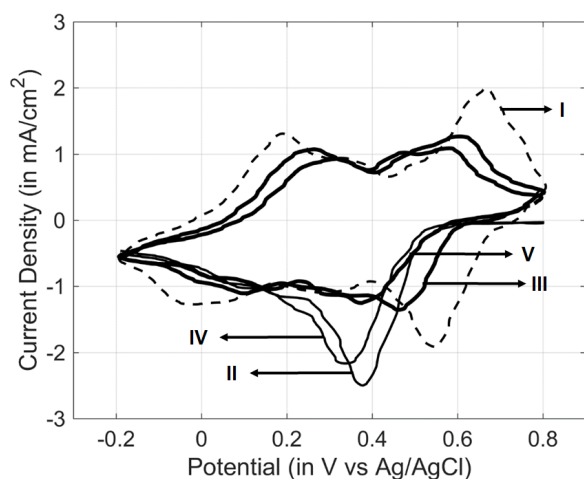


Fig. 6. CV of PANI in 0.1 M HClO₄ at different stages of atomic gold deposition, (I) Initial CV of PANI before deposition, (II) Reduction of AuCl₄⁻ to Au⁰, formation of PANI/Au₁, (III) CV of PANI/Au₁, (IV) Reduction of AuCl₄⁻ to Au⁰, formation of PANI/Au₂, (V) CV of PANI/Au₂ (Scan Rate = 20 mV/sec).

significant difference between nPrOH and iPrOH based on the current density of the two oxidation peaks.

For nPrOH, a higher oxidation peak was obtained at -0.2 V while for iPrOH, the peak was at $+0.2$ V (Fig. 7). Since the CV pattern of nPrOH was different from that of iPrOH, they were distinguishable. The difference can be attributed to the fact that in the electrooxidation of alcohols, the rate-determining step is the deprotonation of the carbon-hydrogen bond [22]. For primary alcohols (e.g. nPrOH), the electrooxidation is more likely to lead to the formation of propionic aldehyde, which may be further oxidized to acids. For secondary alcohols (e.g. iPrOH), the electrooxidation is more likely to lead to ketone as the final product.

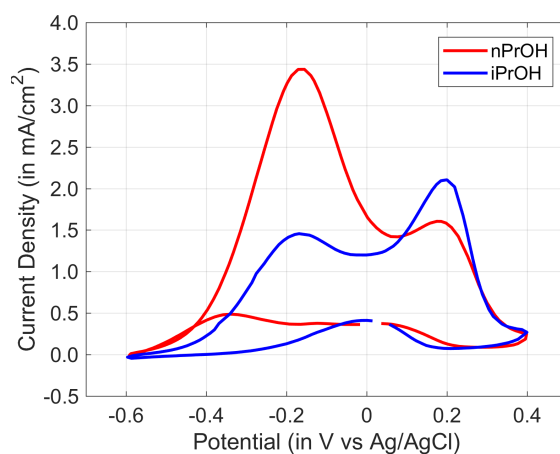


Fig. 7. CV of aq. 0.5 M nPrOH in 1 M KOH (red) and aq. 0.5 M iPrOH in 1 M KOH (blue) (Scan rate: 100 mV/sec).

C. Characteristics of PANI/Au₂ Composite

1) Reproducibility Across Electrodes: The efficacy of the method of growing atomic gold clusters was tested across different Pt substrate and good reproducibility was seen from the CV. However, experiments also showed that there was a change in the current density. This change in density might be due to the variable surface properties of different electrodes, owing to a different amount of PANI polymerized on the surface.

Fig. 8 (a) shows the reproducibility across four electrodes coated with PANI films. Although there were some variations in the current density, discriminable patterns between nPrOH and iPrOH could be seen. In order to overcome the variation in current density, the CV curves were normalized to fit a current density range between 0 to 1. Fig. 8 (b) shows the normalized CV of the four electrodes overlapped with each other. 10 data points at discrete steps of 0.1V were taken from the forward

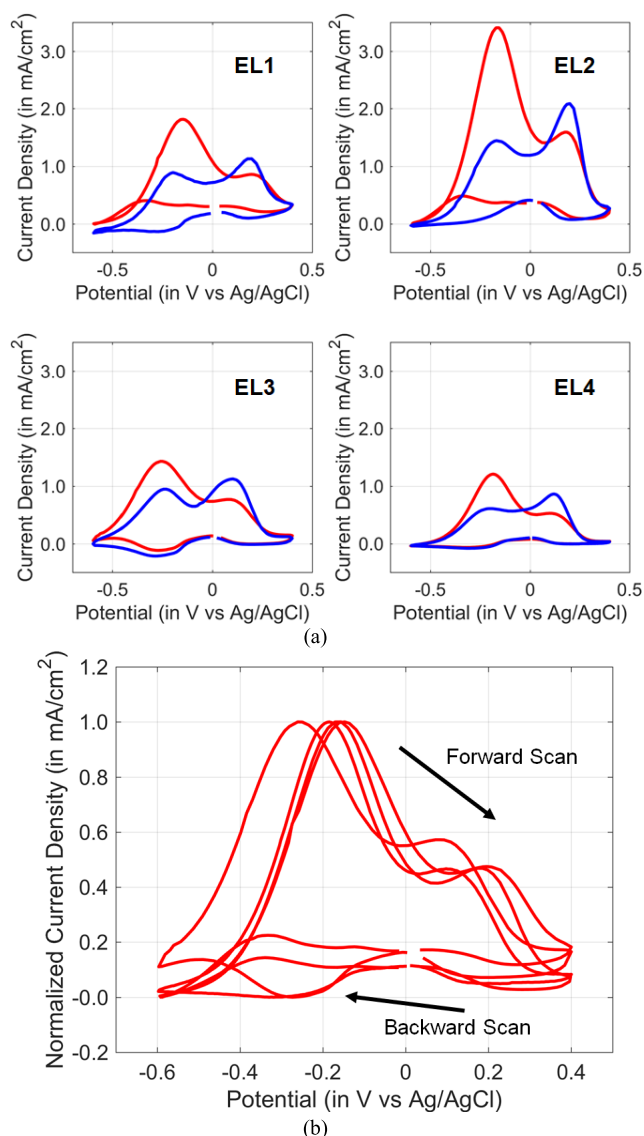


Fig. 8. (a) Reproducibility of CV of PANI/Au₂ composites for nPrOH (red) and iPrOH (blue) across 4 electrodes, (b) Normalization of CV of nPrOH and analysis of overlapping area under forward and backward scans (Scan rate: 100 mV/sec).

scans and backward scans and plotted again. It can be seen that the characteristic shape of PANI/Au₂ still retained after discretization.

In order to further analyze the reproducibility, area under curve was calculated for the forward and backward scans individually for each electrode. Table I shows the Z-score of each electrode for the area under curve in the forward and backward scans. Z-score shows that the statistical data was well within ± 1.96 or 95% confidence interval.

2) **Limit of Detection:** PANI/Au₂ electrode showed a wide detection range from 10^{-5} M to 10^{-2} M with a sensitivity of $42.86 \mu\text{A m}^{-1}\text{cm}^{-2}$ and $10.35 \mu\text{A m}^{-1}\text{cm}^{-2}$ to the detection of aqueous n-propanol and i-propanol, respectively.

3) **Stability of Sensing Material:** The stability of PANI/Au₂ composite was also studied. 30 cycles of CV were taken on a freshly fabricated PANI/Au₂ composite in 0.5 M nPrOH/1M KOH solution. The result showed an ‘activation’ of the reaction sites on PANI. This phenomenon is common for

TABLE I
Z-SCORE OF AREA UNDER CURVE OF FORWARD AND BACKWARD SCANS OF FOUR PANI/Au₂ ELECTRODES

Z-Score	EL1	EL2	EL3	EL4
Z score of area under curve for forward scan $\mu = 0.8121, \sigma = 0.1771$	0.1144	-0.4957	1.3457	-0.9645
Z score of area under curve for backward scan $\mu = 0.2670, \sigma = 0.0526$	1.3847	0.0246	-0.9154	-0.4939

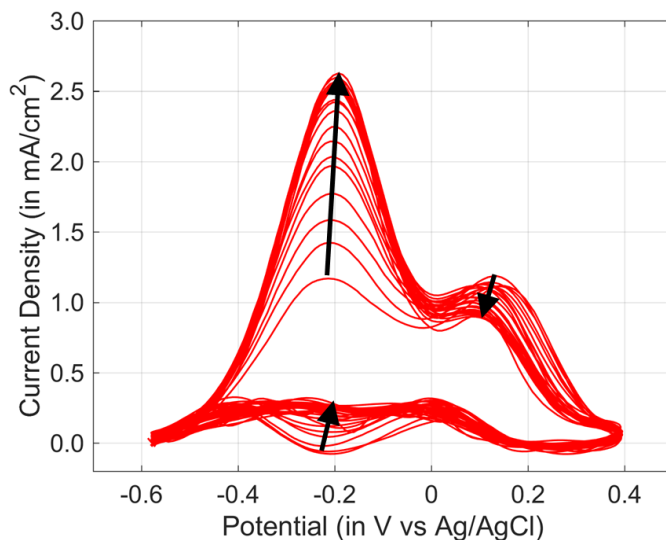


Fig. 9. Stability of PANI/Au₂ composite. 30 continuous CV scans of 0.5 M nPrOH in 1 M KOH showed that the composite reached stability after about 20 scans (Scan rate: 100 mV/sec).

conducting polymers, since due to long polymeric chains, not all reaction sites are available at the first CV scan [22]. However, after 30 cycles a saturation in the CV shape was observed (Fig. 9).

4) **CV Response to Propanols in Gaseous Phase:** The gaseous vapors were bubbled into the electrochemical cell at a given concentration for a fixed period of 5 minutes and CV response was measured. Fig. 10 (a) and (b) show the CV response for nPrOH and iPrOH respectively after bubbling. Discriminable rising peaks could be seen at -0.2 V and $+0.2$ V for nPrOH, however the peak at -0.2 V was more distinct. For iPrOH, both the oxidation peaks at -0.2 V and $+0.2$ V were strong discriminable features.

Figs. 11 (a) and (b) show the plot of standard error of the oxidation peaks for five measurements. It can be seen from the error plots that for nPrOH, the 1st peak grows more than the 2nd peak, whereas for iPrOH, the two oxidation peaks grow together with the 2nd peak relatively higher than the 1st peak.

D. Data Analysis

Further classification could be made between the CV scans obtained at different concentrations of 0%, 30%, 60% and 90% for both nPrOH and iPrOH. In order to analyze this

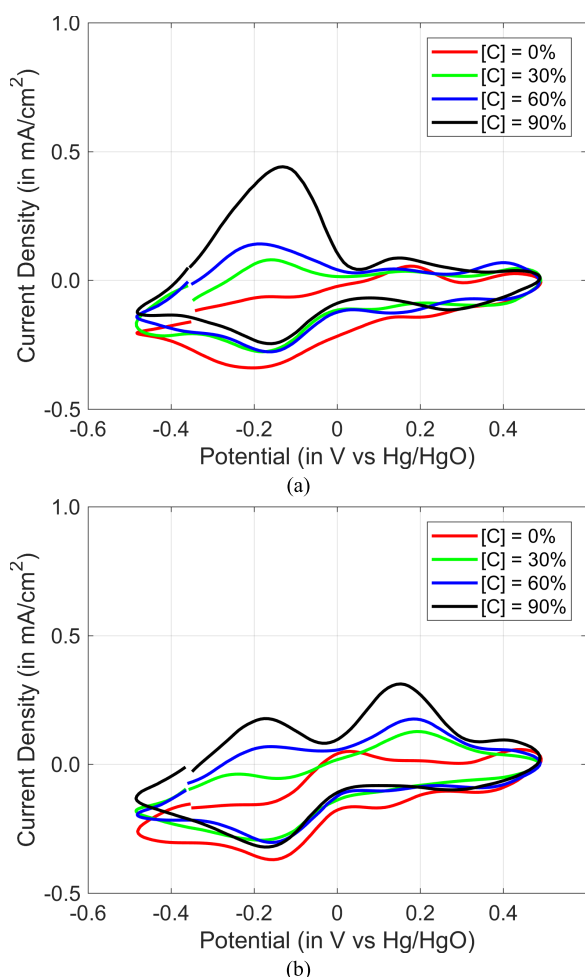


Fig. 10. CV of (a) Gaseous vapors of nPrOH in KOH (b) Gaseous vapors of iPrOH in KOH ([C] = % concentration of full scale 1600 ppm) (Scan Rate = 100 mV/sec).

data obtained in Fig. 10, multidimensional data was generated by slicing the CV curve at steps of 0.1 V (Fig. 12). A total of 20 features (10 features from the forward scan and 10 features from the backward scan) were generated for 8 samples and the data separation was visualized on two dimensions using principal component analysis (PCA).

Fig. 13 shows the PCA plot obtained using covariance matrix. The variance at 1st and 2nd principal component were 77.43 % and 16.07% respectively. The separation between nPrOH and iPrOH was obtained regardless of concentration. The PCA plot also shows that the data converged from high concentration region at 90 % of total concentration to low concentration region at 0% of total concentration.

V. DISCUSSION

Gold clusters containing different number of atoms can be and have been formed in PANI. They exhibit different selectivity for nPrOH and iPrOH. The selective layer of PANI/Au₂ has been selected in order to demonstrate the principle of atomically based selectivity classification between nPrOH and iPrOH in both liquid and gas phase. In this work, most of the working materials and devices were laboratory fabricated.

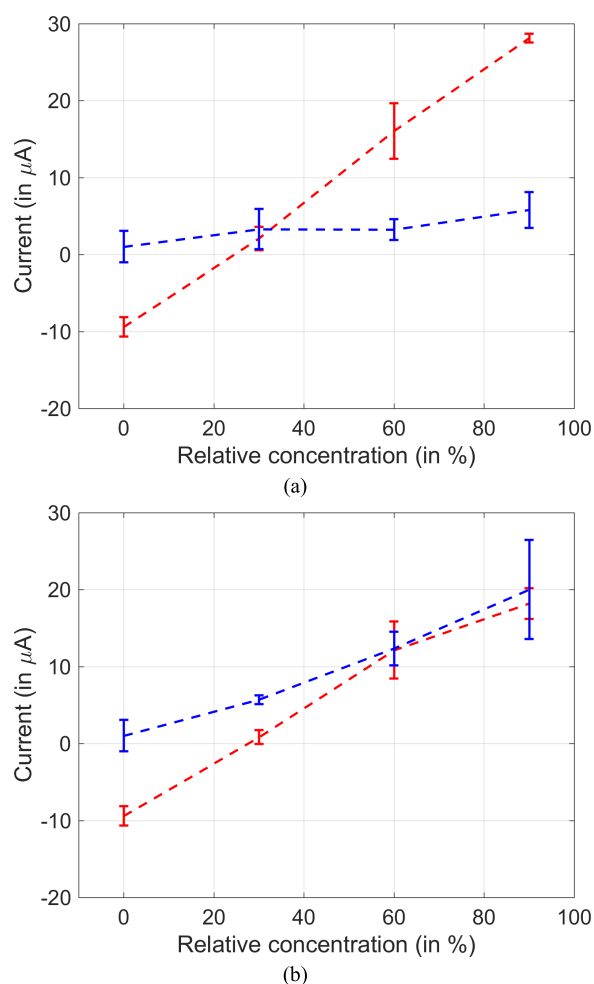


Fig. 11. Plot of standard error of 1st peak recorded at -0.2 V (red) and 2nd peak recorded at $+0.2$ V (blue) for (a) nPrOH and (b) iPrOH.

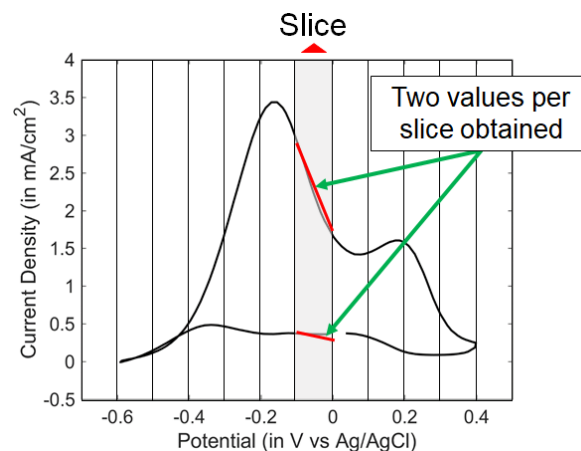


Fig. 12. Data slicing to obtain multidimensional data from CV pattern: 20 dimensions were obtained from the forward and backward scan of CV at steps of 0.1 V. Total of eight samples (CV data at concentration 0%, 30%, 60% & 90% for nPrOH and iPrOH) were obtained for further analysis.

PCA plot shows that values converge from high concentration region to low concentration region; however, the values at zero concentration point do not converge. This offset is due to the background noise of the laboratory-fabricated potentiostat

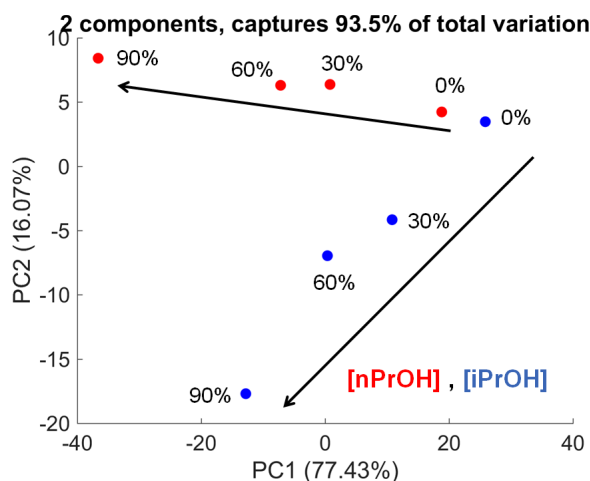


Fig. 13. Principal component analysis (PCA) of multidimensional data obtained from data slicing. PCA shows a good classification between nPrOH and iPrOH and the respective concentrations diverge from low concentration region to high concentration region.

and it needs to be addressed in the future by the use of commercial and high-resolution potentiostat. The detection limit has not yet been optimized. It is of the order of several hundred ppm in air for both nPrOH and iPrOH. This detection limit is still very large when compared with commercially available sensors [12]–[24]. However, the fact that discrimination between two isomers of propanol is possible is most promising. It is assumed that when a target gas is bubbled into the electrochemical cell, gas is completely dissolved into the electrolyte. Since there is always a variation in the dissolution of gas bubbled into the electrolyte, further optimization needs to be done to realize an amperometric gas sensor for real applications.

VI. CONCLUSION

In this paper, PANI composite decorated with bi-atomic gold (PANI/Au₂) was used as the sensing material for classifying between nPrOH and iPrOH vapors. The composite could be successfully used in both liquid and gas phase and discriminable cyclic voltammograms could be obtained at different concentrations of nPrOH and iPrOH. Although this reported work is the with design of amperometric gas sensors using a two atomic gold cluster, higher gold clusters can be formed on PANI to prepare differently modified electrodes to realize a sensing array. There is promising evidence that an atomic metal decorated on a conducting polymer can work as an electro-catalyst. The future direction of this research is to miniaturize the electrode and make the sensing possible at low ppm concentrations. The detection limit may be improved by using microelectrodes as the current density is expected to increase. Then, the mixture quantification method based on active sensing [25] instead of conventional regression techniques will work even if interference gas exists. Moreover, we are interested in studying the selectivity of atomic metal catalysts for various aroma compounds such as geraniol, nerol etc. and their electro-oxidation for the fabrication of smell sensing arrays.

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